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ASSESSMENT OF INDUSTRIAL HAZARDOUS WASTE PRACTICES

INORGANIC CHEMICALS INDUSTRY

VERSAR, INCORPORATED

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16. Abstracts
This report, which covers inorganic chemical manufacturing operations, is one of a series of several which examine land-destined wastes from selected industries. The inorganic chemicals industry (Standard Industrial Classification 281) in 1972 had a total of 1,067 plants producing approximately 112 million metric tons of a wide variety of chemicals with a dollar sales volume of $5.9 billion, and employed 96,000 people. Most of the major plants of this industry are located in the Eastern Seaboard States, the Midwest, and the Gulf Coast States. Approximately 40 million metric tons (dry basis) of land-destined wastes were generated by this industry in 1974, of which 2 million metric tons were considered to be potentially hazardous. Some of the major potentially hazardous constituents identified in the waste streams from this industry include: asbestos, lead, mercury, chlorinated hydrocarbons, fluorides, arsenics, and antimony compounds. The most prevalent method of disposal of potentially hazardous wastes from this industry is some form of land disposal, with about 85 percent of the wastes deposited in landfills, lagoons, and dumps.

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Industrial Gases
Inorganic Pigments
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Solids
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Lead
Mercury
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Landfills
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1.0 INTRODUCTION

This report is the result of a study commissioned by the U.S. Environmental Protection Agency to assess "Industrial Hazardous Waste Practices--Inorganic Chemicals Industry." Concurrently, the EPA pursued similar studies of other industry categories. This program was intended to provide the EPA with as much detailed and pertinent information on the generation, management, treatment, disposal, and costs related to wastes considered to be "potentially hazardous." Such information will be used in developing guidelines or standards for the management of hazardous wastes.

Throughout this report, wherever the terms "hazardous wastes" or "potentially hazardous wastes" are used it should be kept in mind that no final judgments are intended as to such classification. It is recognized and understood that additional information will be required as to the actual fate of such materials in a given "disposal" or "management" environment, before a final definition of "hazardous waste" evolves and is used. As an example, for certain of the waste streams identified in this report the EPA is currently supporting other studies designed to investigate leaching characteristics in various soil and moisture conditions.

Versar Inc., General Technologies Division, began this program for the Environmental Protection Agency (EPA), Office of Solid Waste Management Programs (OSWMP) on 16 January, 1974. It covers standard Industrial Classification (SIC) 281, the inorganic chemicals industry.

The basic objectives of this study are:

(a) Identify those hazardous wastes which are or will be generated by the inorganic chemicals industry;

(b) Describe current practices for treatment and disposal of hazardous wastes;

(c) Determine the control technologies which might be applied to reduce hazards presented by these wastes upon disposal; and

(d) Estimate the cost of control technology implementation.

This report contains the essential elements of the technical information in four major sections:

Section 4.0 - Industrial Characterization

Characterizes the industry with regard to the number, location, size, and production of manufacturing establishments;

Section 5.0 - Waste Characterization

Identifies and quantifies those hazardous wastes which are or will be generated by the inorganic chemical industry;

Section 6.0 - Treatment and Disposal Technology

Describes current practices for treatment and disposal of hazardous wastes and determines the control technologies which might be applied to reduce potential hazards presented by these wastes upon disposal; and

Section 7.0 - Cost Analysis

Estimates the cost and control technology implementation.

The individual elements of each of these phases are presented in detail in their respective sections of this report.

1.1 Program Methodology

1.1.1 Data Acquisition

The data needed for this study was obtained by four different methods. The first was by reviewing published information and data in the technical literature, trade journals, government reports and technical surveys conducted by the industry associations. Some of these references are cited throughout this report.

The second method involved the utilization of data collected during our previous work on effluent limitations guidelines studies on the inorganic chemicals industry for the Effluent Guidelines Division, EPA.

A third method involved trade association participation. The Chlorine Institute in New York City and the Manufacturing Chemists Association in Washington, D. C. were contacted for assistance.

The fourth method of data acquisition was by personal contacts and visits to the various plants and corporate offices of chemical manufacturers. A better and more thorough understanding of the generation of wastes destined for land disposal from chemicals production was obtained through personal interviews.

The results of the overall methodology were fruitful in that information was obtained from:

-visits or other personal contacts with 63 manufacturing facilities
-visits to 4 landfill sites
-visits to 14 waste disposal contractors
-visits to 8 government facilities
-visits to 2 trade associations.

The manufacturers contacted are responsible for over 80 percent of the tonnage of products manufactured in SIC 281 and the 63 manufacturing facilities visited were concentrated among those having potential for producing hazardous wastes destined for land. In all instances the opinions of the manufacturers as to hazardous waste materials generated in their operations were solicited.

The federal government facilities contacted include those belonging to the Atomic Energy Commission, the Department of Commerce, the Department of the Interior, the Environmental Protection Agency, the Interstate Commerce Commission, and the Tennessee Valley Authority.

1.1.2 Data Analysis

The major tasks involved in the data analysis were:

(a) to review the collected data for consistency, sufficiency, and probable accuracy;
(b) to assemble the more reliable data elements into a data base sufficient to allow meaningful projections to be made;
(c) to utilize the data base and subsequent waste factors to allow tabulation of wastes on a state by state, federal region and national basis.

Because of the excellent cooperation of the Chlorine Institute and its member companies, the data base, hazardous waste aggregations and treatment and disposal costs estimates for the Alkalies and Chlorine Industry, SIC 2812, are probably the most accurate of the four industries studied. These are estimated to have an accuracy of ±20 percent.

It was determined that there are no land-destined hazardous wastes emanating from the Industrial Gases Industry, SIC 2813, and therefore the industry characterization data base reported for this industry would have the same standard error of estimate as the 1972 Census of Manufacturers which should be well within ±10 percent.

The accuracy of data reported for the remaining two industries; Inorganic Pigments, SIC 2816 and Industrial Inorganic Chemicals, N.E.C., SIC 2819 is estimated to average about ±40 to 50 percent. In the cases where hard plant data was obtained, the accuracy is estimated to be as good as ±10 to 20 percent. However, where engineering estimates had to be made because of either lack of cooperation or data being withheld to avoid disclosure of confidential information; the accuracy could be considerably less.

1.1.3 Criteria For Determination of Hazardous Wastes

"Hazardous wastes" means any waste or combination of wastes which pose a substantial present or potential hazard to human health or living organisms because such wastes are nondegradable or persistent in nature or because they can be biologically magnified, or because they can be lethal, or because they may otherwise cause or tend to cause detrimental cumulative effects.(69)

Hazardous wastes include materials which are:

(a) toxic or poisonous (producing injury or illness through ingestion, inhalation or absorption through any skin surface);
(b) corrosive (destructive to living tissue);
(c) irritants (induce local inflammatory reaction in living tissue);
(d) strong sensitizers (cause hypersensitivity on living tissue through an allergic or photo-dynamic process);
(e) flammable;
(f) explosive (generate pressure through decomposition, heat or other means);
(g) infectious (represent a potential source of the transmission of diseases to human, domestic animals or wildlife);
(i) radioactive.

Most industrial solid waste streams which contain hazardous constituents also contain significant percentages of non-hazardous constituents. The properties of the severely hazardous constituents and their correspondingly strict disposal requirements overshadow and essentially render

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insignificant the properties and needed disposal restrictions of other constituents in that same waste stream. Other industrial solid waste streams contain no severely hazardous constituents; that is, they contain no environmentally persistent constituents which would have severe impact on the normal functioning of the biota when present in small concentrations. When industrial solid waste streams have no severely hazardous constituents, generally their environmentally acceptable disposal may be handled by following the recommendations for inert and moderately hazardous materials.

The criteria for determining whether a given waste stream constituent should be considered totally innocuous, moderately hazardous or severely hazardous has been based upon precedents set by previous contracting studies and lists of hazardous materials promulgated by EPA. See references 44, 46, 60, 69 and Appendix A references 6, 7, 10, 11, 12, 14, 16, 17, and 19. Initially all waste stream constituents were considered to be potential hazards and then all obviously innocuous items were deleted (e.g., water, sand, brick dust, etc.). The remaining substances were studied in greater depth to determine whether they were toxic, were carcinogens, posed genetic hazards, or were contact, flammability, or explosion hazards when present in the environment in high or low concentrations and whether or not they were environmentally persistent. Those items that were persistent and hazardous or potentially hazardous due to an interaction with the environment at low concentration levels were termed severely hazardous and thus waste streams containing them in appreciable quantities were considered "hazardous" for the present study.

The severely hazardous category includes all substances which are persistent in the environment greater than 3 months and have an acute toxicity of <5 to 500 mg/kg, and/or are known carcinogens.

The moderately hazardous category includes all substances with an acute toxicity of 500 to 5000 mg/kg. Where waste streams contain moderately hazardous materials in high concentrations and with considerable potential for hazard after land disposal, they have been considered as "hazardous" for the purposes of this study. In several instances, calcium fluoride-containing waste streams have been so designated.

2.0 SUMMARY

2.1 Executive Analysis

The industry facilities manufacturing commodities classified under Standard Industrial Classification 281, Industrial Inorganic Chemicals, were found to be currently disposing on land 2×10^6 metric tons of hazardous wastes per year (dry basis) from a total annual industrial waste load of 4×10^7 metric tons (also dry basis). There are four major subcategories of these commodity producers: the *alkalies and chlorine (SIC 2812)* manufacturers that produce such commodities as chlorine, sodium hydroxide, potassium hydroxide, and synthetic soda ash; the *industrial gases (SIC 2813)* manufacturers that produce such commodities as oxygen, nitrogen, hydrogen and carbon dioxide; the *inorganic pigments (SIC 2816)* manufacturers that produce such commodities as titanium dioxide, chrome pigments and iron blues; and the manufacturers of the *industrial inorganic chemicals not elsewhere classified (SIC 2819)* that produce a diversity of commodities such as sulfuric acid, hydrofluoric acid, alum, sodium sulfide, and phosphorus.

The most prominent hazardous wastes for land disposal presently are associated with the *manufacture of alkalies and chlorine (SIC 2812)*. This industry segment has relatively large amounts of the potentially toxic waste materials, mercury, lead and asbestos, which are very persistent. However, the amounts of these wastes generated will decrease significantly in the future as the industry gradually relies less and less on the "mercury cell" process, substitutes the alternative "diaphragm cell" process, and adds improvements in its process equipment. This industry segment has the second largest tonnage of potentially hazardous constituents destined for land of the whole SIC 281 group of industrial inorganic chemical industries. The *mercury cell process* for the manufacture of chlorine is utilized in 28 plants and produces the major amounts of hazardous wastes from this segment. These wastes are from water treatment systems.

The second-ranking industry segment in terms of prominence of land-disposed hazardous waste problems is the *inorganic pigments segment (SIC 2816)* which generates somewhat smaller amounts of hazardous ingredients but larger tonnages of total waste destined for land than SIC 2812. However, these wastes contain several heavy metal elements as the principal hazardous ingredients, which are potentially toxic and very persistent in the environment. The most significant amounts for land disposal arise from 9 plants that *manufacture* *chrome pigments* and 6 plants that *manufacture titanium dioxide by the chloride process*.

The *SIC 2819 industry segment of industrial inorganic chemicals not elsewhere classified* generates the largest tonnages of wastes containing potentially hazardous constituents but is not considered to be as critical a problem as the foregoing two industry segments. This category includes 923 plants and diverse end products and manufacturing processes. The number of potentially "problem" processes and plants which generate potentially hazardous wastes is much smaller than this. As an example, the *manufacture of hydrofluoric acid* accounts for 30 percent of the tonnage of potentially hazardous constituents (primarily fluoride) and about 65 percent of the tonnage of total wastes containing hazardous constituents for this industry segment. Hydrofluoric acid is manufactured at 14 plants. The *manufacture of phosphorus* is also of concern; this results in a smaller amount of waste containing hazardous constituents (20 percent of the total for this SIC code), but accounts for 40 percent of the potentially hazardous constituents. Phosphorus is manufactured at 10 plants. The *manufacture of aluminum fluoride* at 3 plants and the *manufacture of sodium silicofluoride* at 8 plants result in smaller amounts of hazardous constituents and wastes. Although the tonnages of wastes generated by this industry segment (SIC 2819) are large, the hazard presented by the wastes (primarily calcium fluoride) may not be so critical as those from SIC 2812 and SIC 2816. The latent danger in calcium fluoride residue is in acidification and the potential for release of hydrofluoric acid therefrom.

The *industrial gases segment (SIC 2813)* is not a generator of significant amounts of hazardous wastes destined for land. It is important to note that *not all* commodities which could be considered industrial gases on a technical basis are included in this statistical classification. Several are included in SIC 2819 (e.g., sulfur dioxide and fluorine) and SIC 2812 (chlorine).

2.2 General Summary

The industrial hazardous waste practices were assessed for the inorganic chemicals industry in four phases of effort.

Phase I - Industrial Characterization

The industrial inorganic chemicals industry, SIC 281, is subdivided into four major industry categories which were covered in this study:

SIC 2812, Alkalies and Chlorine Industry
SIC 2813, Industrial Gases Industry
SIC 2816, Inorganic Pigments Industry
SIC 2819, Industrial Inorganic Chemicals, Not Elsewhere Classified

The presentation of the data was facilitated by further subdividing each of the major industry categories into their respective 5-digit SIC subcategories. There are seventeen such subcategories in SIC 281 and they are fully characterized with respect to number and distribution of establishments, size on the basis of daily production capacity, age, processes used and yearly production tonnage in Section 4 of this report. A total of 1607 plants producing 112.4 million metric tons of products per year were accounted for in this study.

Phase II - Waste Characterization

The land destined hazardous wastes from the inorganic chemicals industry originates either directly from the manufacturing processes or from air or water effluent treatment. The amount of water in these land-destined waste streams will vary usually between 30 and 80 percent depending on whether the waste is a filter cake or a sludge going to a settling pond. Slurries pumped to deep wells or other land disposal have a greater water content. Therefore, all the waste streams and their hazardous constituents are reported on a dry basis for consistency and are summarized in Table 2-1 which lists currently generated amounts along with projected amounts expected in 1977 and 1983.

Figures 2-1 through 2-4 summarize the current state-by-state distribution of total hazardous waste streams (dry basis) to land disposal from the industries that generate these land-destined wastes. These figures are meant to give the reader a quick picture of the relative amounts of land-destined hazardous wastes emanating from the industrial inorganic chemicals industry and the disposal locations within the U. S. These figures do not indicate the relative degrees of toxicity, flammability, etc., or concentrations of hazardous ingredients, which vary widely.

The waste streams are identified in detail in Section 5 of this report.

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Table 2-1. Summary of Land Destined Hazardous Wastes From Inorganic Chemical Industry (SIC 281)

Major Industry Category	Hazardous Constituents	Metric tons per year to land disposal					
		Haz. Constituents (dry)			Total Haz. Waste Stream (dry/wet)		
		current	1977	1983	current	1977	1983
SIC 2812, Alkalies & Chlorine	asbestos, chlorinated hydrocarbons, lead, mercury	7,000	7,500	4,200	57,000/ 110,000	56,000/ 109,000	45,000/ 89,000
SIC 2813, Industrial Gases	none	0	0	0	0	0	0
SIC 2816, Inorganic Pigments	antimony, arsenic, cadmium, chromium, cyanide, lead, mercury, zinc	4,700	5,800	6,900	160,000/ 350,000	230,000/ 510,000	320,000/ 710,000
SIC 2819, Industrial Inorganic Chemicals, Not Elsewhere Classified	arsenic, chromium, fluoride, nickel, phosphorus, zinc	52,000	53,000	66,000	1,800,000/* 2,900,000	2,000,000/ 3,300,000	2,400,000/ 4,000,000
SIC 281, Inorganic Chemicals Industry	see above	64,000	66,000	77,000	2,000,000/ 3,400,000	2,300,000/ 3,900,000	2,800,000/ 4,800,000

Table 2-2. Summary of Typical Plant Costs for Treatment/Disposal of Hazardous Waste Streams for Environmental Adequacy (Level III)

Industry Subcategory	Product/Process	Treatment/Disposal Cost ($/metric ton of product)	Product Selling Price 1973, ($/metric ton)	Percentage of Treatment Cost to Product Cost
SIC 28121 Chlorine	Diaphragm Cell	0.3	83	0.4
	Mercury Cell	2.-3.		2.4-3.6
	Down's Cell	0.1		0.1
SIC 28161 Titanium Dioxide Pigment	Chloride Process	1.-4.	605-615	0.2-0.7.
SIC 28163 Chrome Colors	Chrome Pigments and Iron Blues	7.-8.	770-1,363 (1971)	0.6-1.0
SIC 28194 Inorganic Acids	Hydrofluoric Acid	11.-15.	616-679	1.7-2.3
SIC 28196 Aluminum Compounds	Aluminum Fluoride	0.6	295 (1971)	0.2
SIC 28197 K and Na Compounds	Sodium Silicofluoride	0.6	175	0.3
SIC 28199 Others N.E.C.	Sodium Dichromate	7.	330	1.8
	Nickel Sulfate	4.	750 (1971)	0.5
	Phosphorus	6.-11.	419	1.4-2.6
	Phosphorus Pentasulfide	0.07	299	0.02
	Phosphorus Trichloride	0.4	292	0.1

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*Does not include 900,000 metric tons of arsenic sulfide wastes from the manufacuture of Sodium Tetraborate Decahydrate. (For details see pages 5-107 - 5-109)

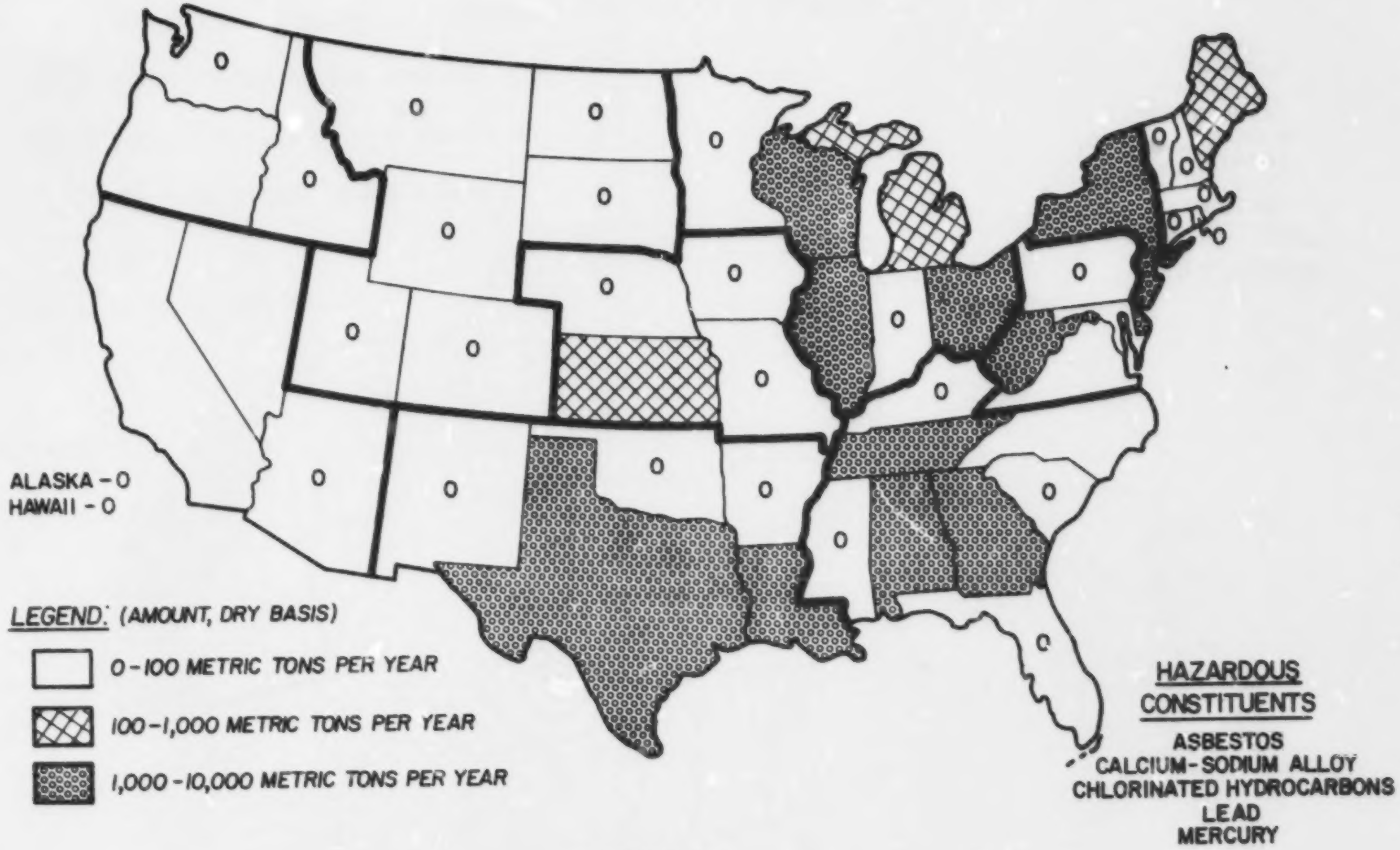
ALASKA - 0
HAWAII - 0
LEGEND: (AMOUNT, DRY BASIS)
0-100 METRIC TONS PER YEAR
100-1,000 METRIC TONS PER YEAR
1,000-10,000 METRIC TONS PER YEAR
HAZARDOUS CONSTITUENTS
ASBESTOS
CALCIUM-SODIUM ALLOY
CHLORINATED HYDROCARBONS
LEAD
MERCURY

FIGURE 2-1

CURRENT HAZARDOUS WASTES TO LAND DISPOSAL
ALKALIES AND CHLORINE (SIC 2812)

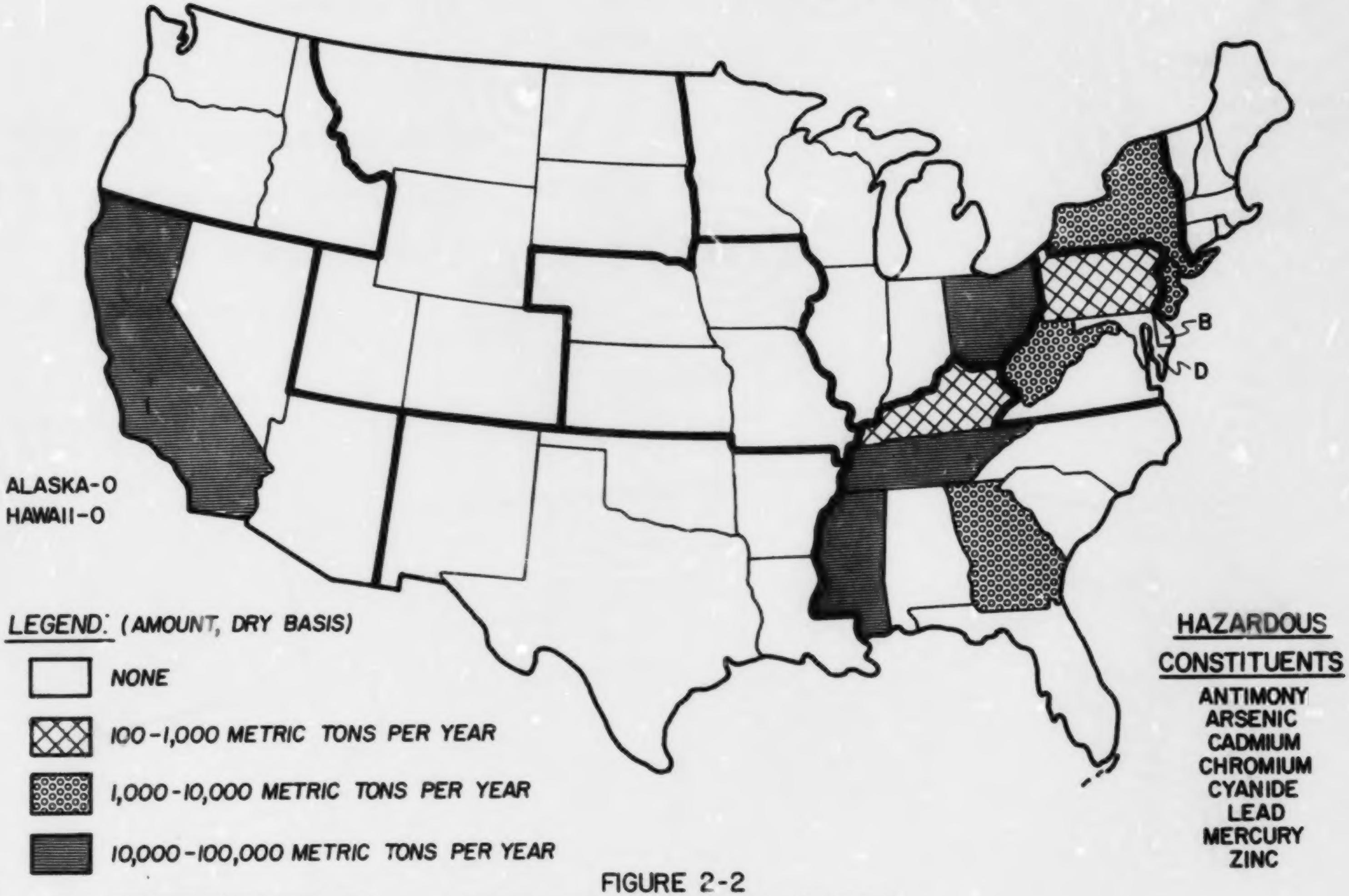

FIGURE 2-2
CURRENT HAZARDOUS WASTES
TO LAND DISPOSAL
INORGANIC PIGMENTS (SIC 2816)

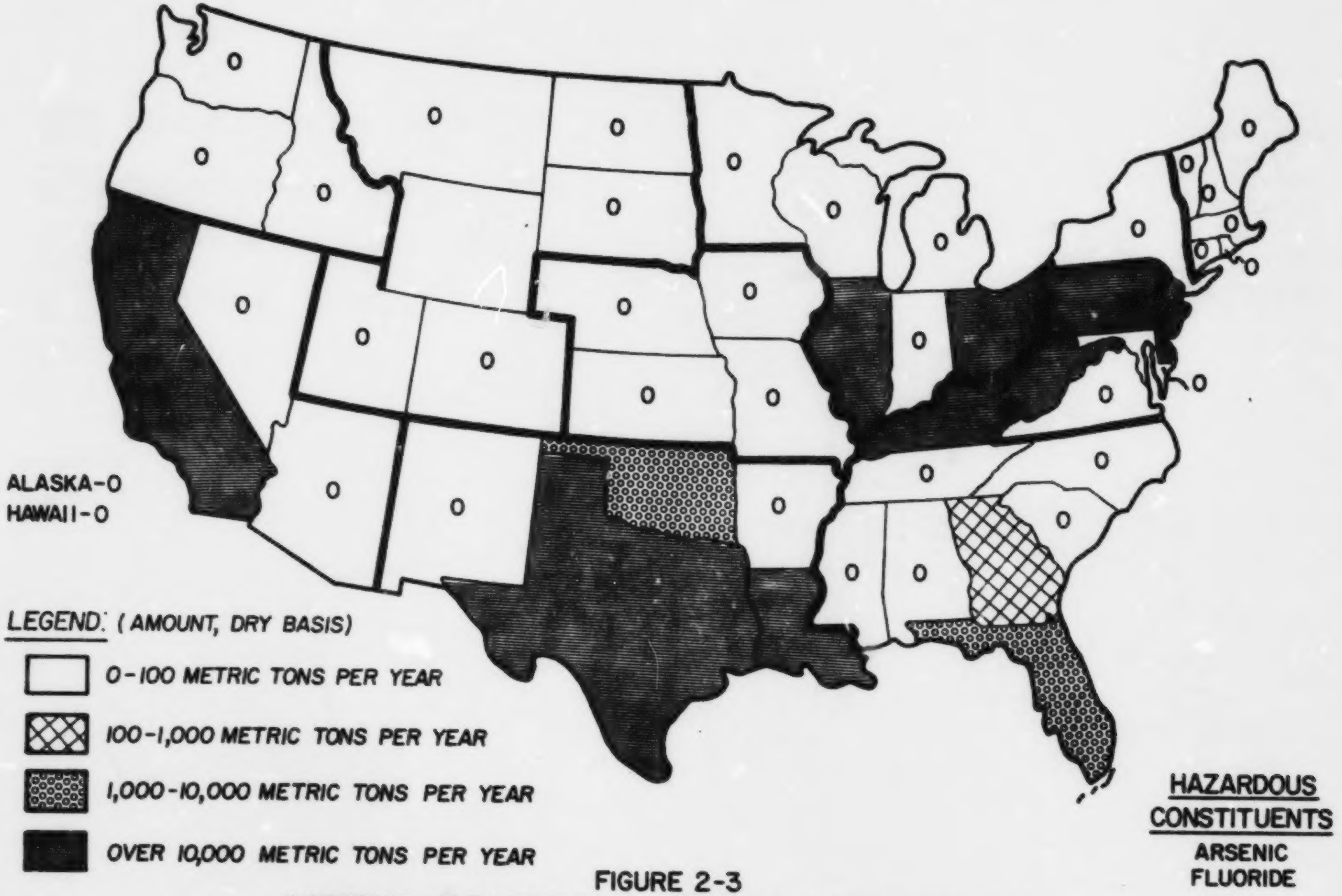
ALASKA-0
HAWAII-0
LEGEND: (AMOUNT, DRY BASIS)
0-100 METRIC TONS PER YEAR
100-1,000 METRIC TONS PER YEAR
1,000-10,000 METRIC TONS PER YEAR
OVER 10,000 METRIC TONS PER YEAR
HAZARDOUS CONSTITUENTS
ARSENIC
FLUORIDE
0
0
0
0
0
0
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FIGURE 2-3
CURRENT HAZARDOUS WASTES TO LAND DISPOSAL
INORGANIC CHEMICALS (SIC 2819)
(EXCLUSIVE OF SIC 28199)

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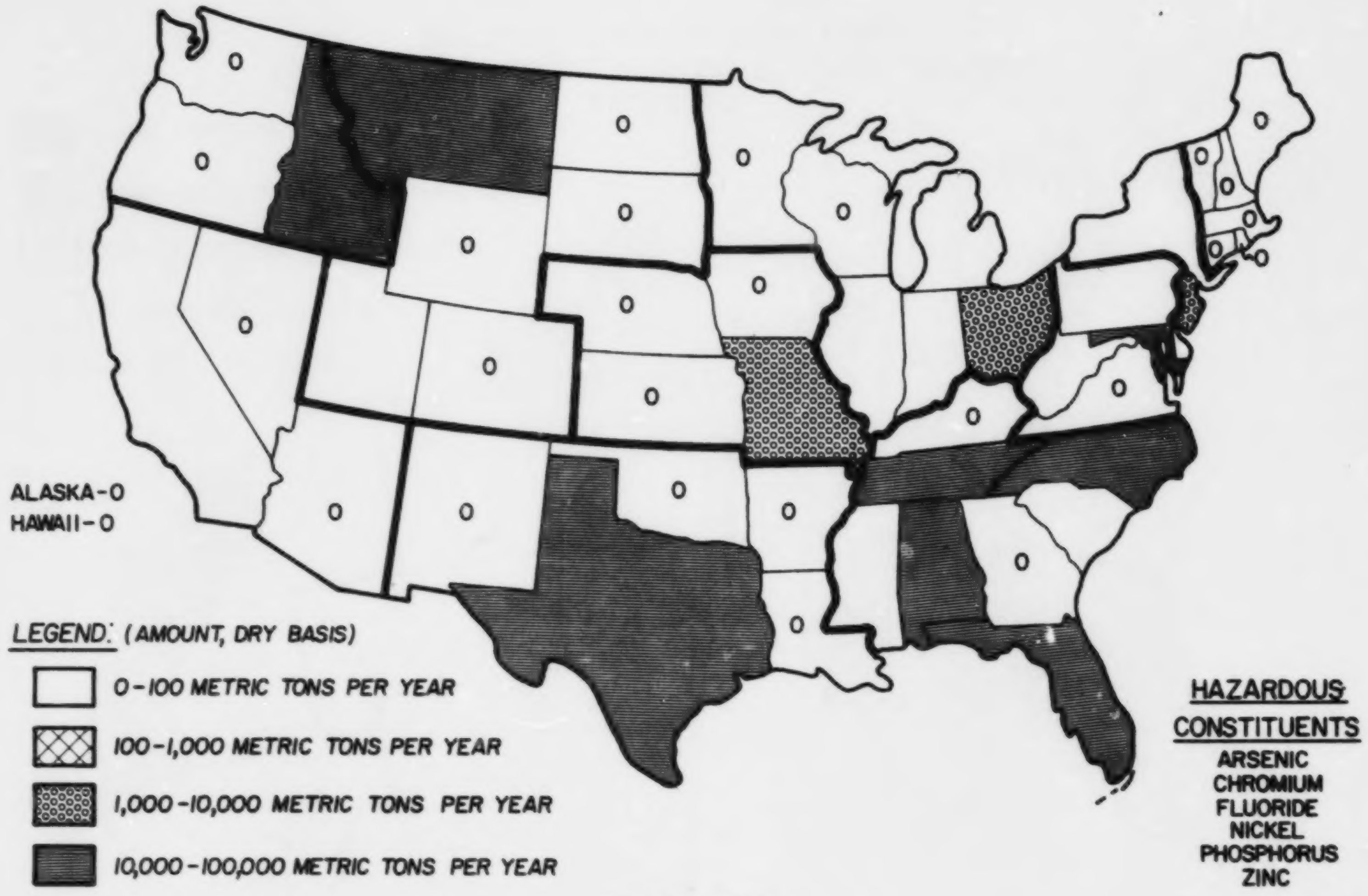
ALASKA-0
HAWAII-0
LEGEND: (AMOUNT, DRY BASIS)
☐ 0-100 METRIC TONS PER YEAR
▨ 100-1,000 METRIC TONS PER YEAR
▒ 1,000-10,000 METRIC TONS PER YEAR
■ 10,000-100,000 METRIC TONS PER YEAR
HAZARDOUS
CONSTITUENTS
ARSENIC
CHROMIUM
FLUORIDE
NICKEL
PHOSPHORUS
ZINC

FIGURE 2-4
CURRENT HAZARDOUS WASTES TO LAND DISPOSAL
INORGANIC CHEMICALS, N.E.C. (SIC 28199)

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Phase III - Treatment and Disposal Technology

Land-destined hazardous wastes from this industry are usually in the form of slurries or wet solids. The technology used in their treatment and disposal depends, for the most part, on:

- the volume of hazardous waste involved
- the chemical composition of the waste
- the local disposal regulations
- the geographical location and
- the availability of disposal land.

Only about 12,000 metric tons per year (or 0.6 percent of the total) of hazardous wastes currently go into secured landfill. On-site storage and disposal (including deep welling) currently accounts for over 75% of the total waste generated by the industry. It is estimated that this percentage will not drop significantly in the foreseeable future. Specifics regarding treatment and disposal technology for hazardous wastes are discussed in Section 6 of this report.

Phase IV - Costs of Treatment and Disposal Technology

Table 2-2 summarizes the typical plant costs for treatment/disposal of hazardous waste streams from the industrial inorganic chemicals industry for environmental adequacy (Level III Technology). It is apparent that the treatment/disposal costs expressed as a percentage of the product selling price are relatively low throughout this industry.

3.0 DISCUSSION OF THE INORGANIC CHEMICALS INDUSTRY

3.1 Introduction

The products of the industry covered in this report are listed under four categories in the 1972 Standard Industrial Classification (SIC) Manual. These are SIC 2812, Alkalies and Chlorine; SIC 2813, Industrial Gases; SIC 2816, Inorganic Pigments and SIC 2819, Industrial Inorganic Chemicals, N.E.C. The production and other overall statistics of the industry broken down into the four SIC codes are published by the Bureau of the Census, U. S. Department of Commerce, in the Census of Manufacturers, Industry Series. Much of the information presented in this overall industry characterization is from the Preliminary Reports, 1972 Census of Manufacturers, which are the most recent ones available.(5) (6) (7) (8)

3.2 Economic Structure and Products of the Alkalies and Chlorine Industry, SIC 2812

The Alkalies and Chlorine Industry includes establishments primarily engaged in manufacturing alkalies and chlorine. The following summarizes the Bureau of Census information on SIC 2812.(5)

In 1972, the value of products shipped and miscellaneous receipts of establishments classified in the Alkalies and Chlorine Industry amounted to $803 million, an increase of 12 percent compared with 1967. Value added by manufacture at $437 million in 1972 was 4 percent above value added in 1967. Average employment in the industry showed a decrease of 31 percent from 1967 to a total of 13 thousand employees in 1972.

Of the $803 million total value of shipments and other receipts of establishments classified in the Alkalies and Chlorine Industry, $262 million were products primary to other industries and $18 million were receipts for miscellaneous activities. The industry shipments of primary products represented 67 percent of the total manufactured products shipments, primary and secondary. This percent, called the "specialization ratio" for the industry, was 67 percent in 1967, also.

The total value of alkalies and chlorine shipped by all producers in 1972 was $801 million of which $523 million, or 65 percent, was shipped by plants classified in Industry 2812, Alkalies and Chlorine, while the remainder was shipped by plants classified in other industries. This percentage, called the "coverage ratio," was 75 percent in 1967.

The types of products, quantities produced and value of shipments for this industry in 1972 are shown in Table 3.1.

3.3 Economic Structure and Products of the Industrial Gases Industry, SIC 2813

The Industrial Gases Industry includes establishments primarily engaged in manufacturing gases for sale in compressed, liquid, and solid forms. The following summarizes the Bureau of Census information on SIC 2813.(6)

Establishments primarily engaged in manufacturing fluorine and sulfur dioxide are classified in industry 2819; household ammonia in industry 2842, other ammonia in industry 2873; and chlorine in industry 2812. Distributors of industrial gases and establishments primarily engaged in shipping liquid oxygen are classified in trade.

In 1972, the value of products shipped and miscellaneous receipts of establishments classified in the Industrial Gases Industry amounted to $673 million, an increase of 14 percent compared with 1967. Value added by manufacture at $463 million in 1972 was 15 percent above value added in 1967. Average employment in the industry showed a decrease of 9 percent from 1967 to a total of 9.4 thousand employees in 1972.

Of the $673 million total value of shipments and other receipts of establishments classified in the Industrial Gases Industry, $31 million were products primary to other industries, and $47 million were receipts for miscellaneous activities. The industry shipments of primary products represented 95 percent of the total manufactured product shipments, primary and secondary. This percent, called the "specialization ratio" for the industry, was 96 percent in 1967.

The total value of industrial gases shipped by all producers in 1972 was $649 million of which $595 million, or 92 percent, was shipped by plants classified in industry 2813, Industrial Gases, while the remainder was shipped by plants classified in other industries. This percentage, called the "coverage ratio," was 89 percent in 1967.

The types of products, quantities produced and value of shipments for this industry in 1972 are shown in Table 3.2.

Table 3-1. Quantity and Value of Products: 1972, SIC 2812
(adapted from Bureau of Census, reference 5)

Product Code	Product	Unit of Measure	Production for all Purposes	Value of Shipments (million dollars)
2812- --	ALKALIES AND CHLORINE, Total	--	(X)	801.4
28121 --	Chlorine, Compressed or Liquefied, Total	--	(X)	208.0
28121 11	Gas	1,000 metric tons	8,955	24.7
28121 15	Liquid	ditto	4,461	182.5
28122 --	Sodium Carbonate (Soda Ash), Total	--	(X)	147.0
	Synthetic (58% Na_2O):			
28122 51	Crude bicarbonate equivalent	1,000 metric tons	3,909	(X)
28122 31	Finished bicarbonate	ditto	112.7	10.6
28122 41	Finished dense ash	ditto	2,114	82.0
28122 45	Finished light ash	ditto	1,676	52.6
28123 --	Sodium Hydroxide (Caustic Soda):	--	(X)	410.5
28123 51 & 70	All processes (100% NaOH)	1,000 metric tons	9,267	(X)
28123 61 & 71	68-74% Liquid	ditto	732	30.6
28123 65 & 75	All other liquid[7]	ditto	7,962	319.9
28122 67 & 77	Dry (all forms)[8]	ditto	431	50.5
28124 --	Other Alkalies, Total	--		
	Potassium hydroxide (caustic potash) (88-92% KOH):			
28124 21	Total liquid	1,000 metric tons	159.2	(X)
28124 22	Liquid	ditto	142.2	21.4
28124 23	Solid	ditto	17.0	3.1
28124 90	Other alkalies	--	(X)	6.0

(X) Not Applicable.

Table 3-2. Quantity and Value of Products: 1972, SIC 2813 (adapted from Bureau of Census, reference 6)

Product Code	Product	Unit of Measure	Production for all Purposes	Value of Shipments (million dollars)
2813- --	INDUSTRIAL GASES, Total	--	(X)	648.8
28132 --	Acetylene, Total	Mil.cu.m.	10,492	94.5
28133 --	Carbon Dioxide, Total	1,000 metric tons	1,343.5	39.2
28133 11	Liquid and gas	ditto	1,065.5	23.4
28133 31	Solid (dry ice)	ditto	278	15.8
28134 --	Elemental Gases and Compressed and Liquefied Gases, N.E.C., Total	--	(X)	479.2
28134 15	Argon, high purity (99.87-100%)	Mil.cu.m.	3,450	33.1
	Helium	ditto	(NA)	(NA)
28134 20	Hydrogen	ditto	53,413	30.3
28134 40	Nitrogen	ditto	175,540	130.3
	Gas	ditto	116,059	33.4
	Liquid	ditto	59,481	96.9
28134 50	Oxygen	ditto	320,343	216.8
	Gas	ditto	(NA)	123.4
	Liquid	ditto	(NA)	93.4
28134 71	Nitrous oxide	Mil. cu.m (STP)	1,159.4	4.5
28134 98	Other industrial gases, n.e.c., including crude argon, carbon dioxide produced and transferred for further processing, and crude and high purity helium produced in privately owned plants	--	(X)	50.1
28130 00	Industrial gases, n.s.k., as reported in census of manufactures for companies with 10 employees or more	--	(X)	25.2
28130 02	Industrial gases, n.s.k., as reported in census of manufactures for companies with less than 10 employees	--	(X)	3.5

(X) Not applicable. (NA) Not available. n.e.c. Not elsewhere classified. n.s.k. Not specified by kind.

3.4 Economic Structure and Products of the Inorganic Pigments Industry, SIC 2816

The Inorganic Pigments Industry includes establishments primarily engaged in manufacturing inorganic pigments. Important products of this industry include black pigments, white pigments, and color pigments.

Organic color pigments, except animal black and bone black, are classified in industry 2865. The following summarizes the Bureau of Census information on SIC 2816.(7)

In 1972, the value of products shipped and miscellaneous receipts of establishments classified in the Inorganic Pigments Industry amounted to $793 million, an increase of 44 percent compared with 1967. Value added by manufacture at $384 million in 1972 was 22 percent above value added in 1967. Average employment in the industry showed an increase of 1 percent from 1967 to a total of 12.7 thousand employees in 1972.

Of the $793 million total value of shipments and other receipts of establishments classified in the Inorganic Pigments Industry, $103 million were products primary to other industries, and $34 million were receipts for miscellaneous activities. The industry shipments of primary products represented 86 percent of the total manufactured product shipments, primary and secondary. This percent, called the "specialization ratio" for the industry, was 90 percent in 1967.

The total value of inorganic pigments shipped by all producers in 1972 was $756 million of which $656 million, or 87 percent, was shipped by plants classified in industry 2816, Inorganic Pigments, while the remainder was shipped by plants classified in other industries. This percentage, called the "coverage ratio," was 84 percent in 1967.

The types of products, quantities produced and value of shipments for this industry in 1972 are shown in Table 3.3.

3.5 Economic Structure and Products of the Industrial Inorganic Chemicals, N.E.C., Industry, SIC 2819

The Industrial Inorganic Chemicals, N.E.C., Industry includes establishments primarily engaged in manufacturing industrial inorganic chemicals, n.e.c. Important products of this industry include inorganic salts of sodium (excluding refined sodium chloride), potassium, aluminum, calcium, chromium, magnesium, mercury, nickel, silver, tin; inorganic compounds such as alums, calcium carbide, hydrogen

Table 3-3. Quantity and Value of Products: 1972, SIC 2816 (adapted from Bureau of Census, reference 7)

Product Code	Product	Unit of Measure	for all Purposes	Value of Shipments (million dollars)
2816- --	INORGANIC PIGMENTS, Total	--	(X)	755.7
28161 11	Titanium Pigments, Composite and Pure (100% TiO_2), Total	1,000 metric tons	639.7	355.3
28162 —	Other White Opaque Pigments	--	(X)	101.4
28162 13	White lead, basic carbonate and sulfate, excluding white lead in oil	1,000 metric tons	16.6	5.0
	Zinc oxide pigments:			
28162 21	Lead-free zinc oxide	ditto	212.9	79.2
28162 25	Leaded zinc oxide	ditto	(D)	*
28162 98	All other white opaque pigments, including antimony oxide, lithopone, and pure zinc sulfide	--	(X)	14.5
28162 00	Other white opaque pigments, n.s.k.	--	(X)	2.9
28163 --	Chrome Colors and Other Inorganic Pigments	--	(X)	284.5
28163 10	Chrome colors, Total	--	(X)	59.1
28163 11	Chrome green (chrome yellow and iron blue) (C.P.)	1,000 metric tons	(D)	(D)
28163 13	Chrome oxide green (C.P.)	ditto	5.6	5.9
28163 15	Chrome yellow and organce (C.P.)	ditto	30.6	24.5
28163 17	Molybdate chrome orange (C.P.)	ditto	11.2	13.7
28163 18	Zinc yellow (zinc chromate) (C.P.)	ditto	5.2	4.6
28163 19	Other chrome colors (C.P.)	ditto	(S)	(S)
28163 27	White extender pigments, including barytes, blanc fixe, and whiting	ditto	(S)	14.2
	Color pigments other than chrome colors and lakes and toners:			
28163 31	Iron oxide pigments	ditto	(S)	40.1
	Colored lead pigments:			
28163 41	Red lead	ditto	24.0	11.1
28163 45	Litharge	ditto	162	49.3
28163 51	Iron blues (Prussian blue, milori blue, etc.): As reported in census of manufactures	ditto	4.8	6.5
28163 61	Pearl essence	ditto	(D)	(D)
28163 88	Carbon blacks (bone and lamp), excluding furnace and channel carbon black and charcoal	ditto	2	.9
28163 91	Ceramic colors	ditto	(S)	36.5
28163 98	All other color pigments, including ultramarine blue (excluding organic pigments, lakes, and toners)	--	(X)	58.9
28163 00	Chrome colors and other inorganic pigments, n.s.k.	--	(X)	7.9
28160 00	Inorganic pigments, n.s.k., for companies with 10 employees or more	--	(X)	9.0
28160 02	Inorganic pigments, n.s.k., for companies with less than 10 employees	--	(X)	5.1

* Included with product code 28163 98. (X) Not applicable (S) Withheld - poor data. (D) Withheld to avoid disclosing figures for individual companies.

peroxide, sodium silicate, ammonia compounds (except fertilizers), rare earth metal salts and elemental bromine, fluorine, iodine, phosphorus, and alkali metals (sodium, potassium, lithium, etc.). Establishments primarily engaged in mining, milling, or otherwise preparing natural potassium, sodium, or boron compounds (other than common salt) are classified in industry 1474. Establishments primarily engaged in manufacturing household bleaches are classified in industry 2842; phosphoric acid in industry 2874; and nitric acid, anhydrous ammonia and other nitrogenous fertilizer materials in industry 2873. The following summarizes the Bureau of Census information on SIC 2819.(8)

In 1972, the value of products shipped and miscellaneous receipts of establishments classified in industry 2819 amounted to $3,658 million. The 2819 industry reported value added by manufacture of $1,997 million and employment of 61 thousand in 1972.

Of the $3,658 million total value of shipments and other receipts of establishments classified in the 2819 industry, $323 million were products primary to other industries, and $1,032 million were receipts for miscellaneous activities. The industry shipments of primary products represented 88 percent of the total manufactured product shipments, primary and secondary. This percentage is called the "specialization ratio."

The total value of industrial inorganic chemicals, n.e.c., shipped by all producers in 1972 was $2,946 million of which $2,303 million or 78 percent, was shipped by plants classified in industry 2819, Industrial Inorganic Chemicals, N.E.C., while the remainder was shipped by plants classified in other industries. This percentage is called the "coverage ratio."

The types of products, quantities produced and value of shipments for this industry in 1972 are shown in Table 3.4.

3.6 Individual Chemical Processes and Waste Streams

The processes by which the various chemicals covered in this report are manufactured and their associated waste streams are discussed in detail in Section 5 of this report.

The inorganic chemicals industry is further characterized by the number of plants, age of plants, size of plants and location of plants in Section 4 of this report.

Table 3-4. Quantity and Value of Products: 1972, SIC 2819 (adapted from Bureau of Census, reference 8)

Product Code	Product	Unit of Measure	Production for all Purposes	Value of Shipments (million dollars)
2819- --	INDUSTRIAL INORGANIC CHEMICALS, N.E.C., Total	--	(X)	2,946.5
28193 --	Sulfuric Acid, Total	1,000 metric tons	28,388.8	248.1
	Contact acid:			
28193 11	Oleum under 40%	ditto	1,706.9	31.4
28193 15	Oleum 40%	ditto	484.9	(D)
28193 17	Oleum over 40%	ditto	218.2	(D)
28193 31	Other then oleum grades	ditto	25,849.3	205.6
28193 51	Chamber acid	ditto	129.5	0.4
28193 71	Spent acid used in fortification in contact units and included in production reported above, including acid from own production or received from outside sources	--	1,118.1	(X)
28194 --	Inorganic Acids, except Nitric and Sulfuric, Total	--	(X)	153.0
28194 11	Boric (boraic) (100% H_3BO_3)	1,000 metric tons	110.2	11.1
28194 31	Chromic acid (100% CrO_3)	ditto	24.6	15.8
	Hydrochloric, including anhydrous (100% HCl)	ditto ditto	2,088.3	36.9
28194 41	From salt	ditto	103.2	4.2
28194 45	From chlorine	ditto	93.3	3.7
28194 47	Byproduct and other	ditto	1,891.8	29.0
28194 51	Hydrocyanic, including anhydrous (100% HCN)	ditto	123.2	*
	Hydrofluoric (100% HF):			
28194 61	Anhydrous	ditto	218.7	52.7
28194 65	Technical	ditto	16.1	7.9
28194 67	Mixed (sulfuric and nitric)	ditto	185.5	*
28194 98	Other inorganic acid acids, n.e.c.	ditto	(X)	28.9
28195 --	Aluminum Oxide, Except Alumina (100% Al_2O_3), Total	1,000 metric tons	5,624.2	387.9
28196 --	Other Aluminum Compounds, Total	--	(X)	174.2
	Chloride:			
28196 11	Liquid (32° Be[1])	1,000 metric tons	(D)	(D)
28196 15	Crystal (32° Be[1])	ditto	(D)	(D)
28196 17	Anhydrous (100% $AlCl_3$)	ditto	30.3	8.9
28196 25	Hydroxide: trihydrate (100% $Al_2O_3 \cdot 3H_2O$)	ditto	480.1	47.2
28196 27	Fluoride (technical)	ditto	126	36.1
	Sulfate:			
28196 51	Commercial (17% Al_2O_3)	ditto	1,139.5	51.6
28196 55	Iron free (17% Al_2O_3)	ditto	64.6	3.0
28196 71	Other inorganic aluminum compounds, including sodium aluminate, light aluminum hydroxide, cryolite, and alums	--	(X)	27.3
28197 --	Potassium and Sodium Compounds (Except Bleaches, Alkalies, and Alums), Total	--	(X)	501.1
	Potassium compounds, n.e.c.			
28197 13	Iodide (100% KI)	1,000 metric tons	.99	4.5

(X) Not applicable. (D) Withheld to avoid disclosing individual company data. * Included with product code 28163.

Table 3-4. Quantity and Value of Products: 1972, SIC 2819 (adapted from Bureau of Census, reference 8)

Product Code	Product	Unit of Measure	Production for all Purposes	Value of Shipments (million dollars)
2819- --	INDUSTRIAL INORGANIC CHEMICALS, N.E.C., Total	--	(X)	2,946.5
28193 --	Sulfuric Acid, Total	1,000 metric tons	28,368.8	248.1
	Contact acid:			
28193 11	Oleum under 40%	ditto	1,706.9	31.4
28193 15	Oleum 40%	ditto	484.9	(D)
28193 17	Oleum over 40%	ditto	218.2	(D)
28193 31	Other than oleum grades	ditto	25,849.3	205.6
28193 51	Chamber acid	ditto	129.5	0.4
28193 71	Spent acid used in fortification in contact units and included in production reported above, including acid from own production or received from outside sources	--	1,118.1	(X)
28194 --	Inorganic Acids, except Nitric and Sulfuric, Total	--	(X)	153.3
28194 11	Boric (boracic) (100% H_3BO_3)	1,000 metric tons	110.2	11.1
28194 31	Chromic acid (100% CrO_3)	ditto	24.6	15.8
	Hydrochloric, including anhydrous (100% HCl)	ditto ditto	2,088.3	36.9
28194 41	From salt	ditto	103.2	4.2
28194 45	From chlorine	ditto	93.3	3.7
28194 47	Byproduct and other	ditto	1,891.8	29.0
28194 51	Hydrocyanic, including anhydrous (100% HCN)	ditto	123.2	*
	Hydrofluoric (100% HF):			
28194 61	Anhydrous	ditto	218.7	52.7
28194 65	Technical	ditto	16.1	7.9
28194 67	Mixed (sulfuric and nitric)	ditto	125.5	*
28194 98	Other inorganic acid acids, n.e.c.	ditto	(X)	28.9
28195 --	Aluminum Oxide, Except Alumina (100% Al_2O_3), Total	1,000 metric tons	5,624.2	387.9
28196 --	Other Aluminum Compounds, Total	--	(X)	174.2
	Chloride:			
28196 11	Liquid (32° Be^1)	1,000 metric tons	(D)	(D)
28196 15	Crystal (32° Be^1)	ditto	(D)	(D)
28196 17	Anhydrous (100% $AlCl_3$)	ditto	33.3	8.9
28196 25	Hydroxide: trihydrate (100% $Al_2O_3 \cdot 3H_2O$)	ditto	480.1	47.2
28196 27	Fluoride (technical)	ditto	126	36.1
	Sulfate:			
28196 51	Commercial (17% Al_2O_3)	ditto	1,133.5	51.6
28196 55	Iron free (17% Al_2O_3)	ditto	64.6	3.0
28196 71	Other inorganic aluminum compounds, including sodium aluminate, light aluminum hydroxide, cryolite, and alums	--	(X)	27.3
28197 --	Potassium and Sodium Compounds (Except Bleaches, Alkalies, and Alums), Total	--	(X)	501.1
	Potassium compounds, n.e.c.			
28197 13	Iodide (100% KI)	1,000 metric tons	.99	4.5

(X) Not applicable. (D) Withheld to avoid disclosing individual company data. * Included with product code 28163.

Table 3-4. Quantity and Value of Products: 1972, SIC 2819 - continued (adapted from Bureau of Census, reference 8)

Product Code	Product	Unit of Measure	Production for all Purposes	Value of Shipments (million dollars)
28197 16	Sulfate (100% K_2SO_4)	ditto	364.9	16.4
28197 18	Tetrapotassium pyrophosphate (100% $K_2P_2O_7$)	ditto	44.6	5.0
28197 17	Other potassium salts and compounds, n.e.c.	--	(X)	90.1
28197 21	Sodium (metal) (100% Na)	1,000 metric tons	145.6	37.2
	Sodium compounds, n.e.c.:			
28197 24	Borate (borax)	ditto	498.5	10.4
28197 27	Chlorate (100% $NaClO_3$)	ditto	175.8	16.7
28197 28	Fluoride	ditto	5.6	2.2
28197 29	Hydrosulfide (sodium sulfhydrate) (100% NaSH)	ditto	22.8	2.7
28197 30	Hydrosulfite (100% $Na_2S_2O_4$)	ditto	42.4	20.9
	Phosphate:			
28197 32	Monobasic (100% NaH_2PO_4)	ditto	30.5	7.1
28197 33	Dibasic (100% Na_2HPO_4)	ditto	18.9	4.4
28197 34	Tribasic (100% Na_3PO_4)	ditto	52.5	10.5
28197 35	Tetrabasic (100% $Na_4P_2O_7$)	ditto	42.1	8.7
28197 36	Meta (100% $NaPO_3$)	ditto	72.1	16.7
28197 37	Acid pyro (100% $Na_2H_2P_2O_7$)	ditto	24.7	6.7
28197 38	Tripoly (100% $Na_5P_3O_{10}$)	ditto	936.7	143.6
	Silicates:			
28197 41	Soluble silicate glass (water glass) solid and liquid (anhydrous)	1,000 metric tons	599.2	45.3
28197 43	Metasilicate (100% $Na_2SiO_3 \cdot 5H_2O$)	ditto	251.1	21.3
28197 51	Silicofluoride (100% Na_2SiF_6)	ditto	52.1	6.3
	Sulfate:			
28197 61	High purity (refined) (100% Na_2SO_4)	ditto	726.1	17.0
28197 65	Low purity (99% or less Na_2SO_4) (100% Na_2SO_4)	ditto	477.5	11.1
28197 67	Glauber's salt (100% $Na_2SO_4 \cdot 10H_2O$)	ditto	477.5	11.1
	Sulfide:			
28197 81	Crystal	ditto	130.1	4.9
28197 82	Concentrated (60-62% Na_2S)	ditto	130.1	4.9
28197 83	Other, including liquid and crystal (60-6% Na_2S)	ditto	130.1	4.9
28197 84	Sulfite (100% Na_2SO_4)	ditto	202.5	9.4
28197 85	Thiosulfate (hypo) (100% $Na_2S_2O_3 \cdot 5H_2O$)	ditto	19.6	2.7
28197 87	Other sodium compounds, n.e.c.	--	(X)	130.9
28198 --	Chemical Catalytic Preparations, Total	--	(X)	167.5
28199 --	Other Inorganic Chemicals, H.E.C., Total	--	(X)	1,303.4
28199 01	Reagent and high purity grades of inorganic chemicals refined from purchased technical grades	--	(X)	44.4
28199 02	Antimony compounds, (excluding pigment grades)	--	(X)	2.3
	Barium compounds:			
28199 04	Carbonate (precipitated) (100% $BaCO_3$)	1,000 metric tons	63.7	8.3
28199 06	Other barium compounds	--	(X)	8.9
	Bismuth compounds:			
28199 07	Subcarbonate (100% $(Bi_2O_2CO_3) \cdot H_2O$)	1,000 metric tons	(Z)	0.3
28199 09	Other bismuth compounds	--	(X)	2.2
28199 10	Bromine (100% Br)	1,000 metric tons	(X)	14.1
28199 11	Cadium compounds	--	(X)	8.4
	Calcium compounds:			
	Calcium compounds:			
28199 12	Carbide (commercial)	1,000 metric tons	447.5	24.6
28199 13	Carbonate (precipitated) (100% $CaCO_3$)	ditto	200.4	12.1
	Chloride:			
28199 14	Solid, excluding flake (73-75% $CaCl_2$)	ditto	589.7	26.1
28199 15	Flake (77-80% $CaCl_2$)	ditto	589.7	26.1
28199 16	Liquid (40-45% $CaCl_2$)	ditto	470.4	4.9
28199 41	Calcium hypochlorite (high test) (70% avail. Cl)	1,000 metric tons	(D)	(D)
	Phosphate:			
	Dibasic:	ditto	627.5	
28199 19	Animal feed grades	ditto	627.5	61.8
28199 20	Other grades (except fertilizer grades)			61.8
28199 18	Monobasic	--	(X)	9.7
28199 21	Tribasic	--	(X)	9.7

(X) Not applicable. (D) Withheld to avoid disclosing individual company data. (Z) Less than half of the unit of measure shown.

Table 3-4. Quantity and Value of Products: 1972, SIC 2819 - continued (adapted from Bureau of Census, reference 8)

Product Code	Product	Unit of Measure	Production for all Purposes	Value of Shipments (million dollars)
28199 23	Other inorganic calcium compounds	--	(X)	48.5
	Carbon, activated:			
28199 24	Decolorizing	1,000 metric tons	79.3	29.3
28199 26	Water purification	ditto	79.3	29.3
	Chromium compounds:			
	Bichromates and chromates:			
28199 29 & 31	Sodium bichromate and chromate (hydrous)	ditto	133.1	24.5
28199 32	Other chromium compounds including	--	(X)	8.9
	potassium bichromate and chromate (hydrous) (excluding chrome colors)	--	(X)	8.9
28199 33	Cobalt compounds	--	(X)	10.8
	Copper compounds:			
28199 34	Cupric oxide (100% CuO)	1,000 metric tons	1.6	1.4
28199 35	Cuprous oxide (100% Cu_2O)	ditto	1.7	2.0
28199 36	Copper sulfate (100% $CuSO_4 \cdot 5H_2O$)	ditto	(D)	(D)
28199 37	Other copper compounds (including copper cyanide)	--	(X)	23.5
28199 39	Hydrogen peroxide	1,000 metric tons	66.5	31.0
28199 40	Iodine, crude or resublimed (100% I)	1,000 metric tons	(S)	(S)
	Iron compounds:			
28199 42	Ferric chloride (100% $FeCl_3$)	1,000 metric tons	69.6	5.6
28199 43	Ferrous sulfate (100% $FeSO_4 \cdot 7H_2O$)	ditto	(D)	(D)
28199 44	Other iron compounds	--	(X)	3.8
	Lead Compounds:			
28199 45	Nitrate	--	(X)	9.0
28199 47	Other lead compounds (excluding pigment grade)	--	(X)	9.0
	Magnesium compounds:			
28199 48	Sulfate, including Epsom salts (100% $MgSO_4$)	--	(X)	41.6
28199 49	Other magnesium compounds	--	(X)	41.6
	Manganese compounds:			
28199 50	Sulfate (100% $MnSO_4 \cdot 4H_2O$)	1,000 metric tons	28.7	3.1
28199 52	Other manganese compounds, including potassium and other permanganates and manganese dioxide, battery grade	--	(X)	13.1
28199 53	Mercury and compounds:			
	Mercury, redistilled (lb)	1,000 metric tons	313.1	1.3
28199 55	Other mercuric compounds, except mercuric fulminate and medicinal grades	--	(X)	2.1
28199 90	Molybdenum, platinum, radium, strontium, tantalum, thallium, and tungsten compounds	--	(X)	107.6
	Nickel compounds:			
28199 56	Sulfate (100%, $NiSO_4 \cdot 6H_2O$)	1,000 metric tons	9.3	6.9
28199 57	Other nickel compounds	--	(X)	6.9
	Phosphorus and compounds:			
	Phosphorus elemental:			
28199 58	White (yellow) (technical)	1,000 metric tons	504.2	195.1
28199 59	Red (technical)	ditto	31.4	4.2
28199 60	Oxychloride (100% $POCl_3$)	ditto	31.4	4.2
28199 63	Trichloride (chloride) (100% PCl_3)	ditto	57.7	6.1
28199 61	Pentasulfide (100% P_2S_5)	ditto	55.5	10.9
28199 65	Rare earth compounds	--	(X)	20.1
28199 66	Selenium compounds	--	(X)	1.8
	Silica gel:			
28199 68	Butadiene catalyst grade	--	(X)	64.4
28199 69	Desicant grade	--	(X)	64.4
28199 70	Aviation gas catalyst grade	--	(X)	64.4
	Silver compounds:			
28199 71	Cynnide (100% $AgCN$)	28.35 kg.	36.8 kg	2.0
28199 72	Nitrate (100% $AgNo_3$)	ditto	2,832.7 kg.	8.4
28199 73	Other silver compounds	--	(X)	14.3

(X) Not applicable. (D) Withheld to avoid disclosing individual company data. (S) Does not meet publications standards.

Table 3-4. Quantity and Value of Products: 1972, SIC 2819 - continued (adapted from Bureau of Census, reference 8)

Product Code	Product	Unit of Measure	Production for all Purposes	Value of Shipments (million dollars)
28199 74	Sulfur, recovered elemental	1,016 metric tons	1,958.8	29.8
	Sulfur compounds:			
28199 75	Dioxide (produced for sale) (100% SO_2)	ditto	101.8	5.4
26199 77	Other sulfur compounds (including sulfur chloride)	--	(X)	10.9
	Tin compounds:			
28199 80	Oxide (stannic) (100% SnO_2)	1,000 metric tons	(D)	(D)
28199 81	Other tin compounds (including stannic and stannous chloride)	--	(X)	19.8
	Zinc compounds:			
28199 87	Sulfate (100% $ZnSO_4 \cdot 7H_2O$)	1,000 metric tons	40.5	6.8
28199 88	Other zinc compounds excluding pigment grades	--	(X)	13.6
28199 91	Radioactive isotopes shipped from non-AEC plants producing isotopes	--	(X)	37.9
28199 92	Radiation sources and other radioactive materials produced from purchased isotopes	--	(X)	15.9
28199 94 & 95	Industrial bleaches including liquid lime bleaches	--	(X)	5.1
28199 98	All other inorganic chemicals, n.e.c.	--	(X)	214.7
28199 00	Industrial inorganic chemicals, n.s.k., reported in census of manufactures, for companies with 10 employees or more	--	(X)	18.8
28199 02	Industrial inorganic chemicals, n.s.k., reported in census of manufactures, for companies with less than 10 employees	--	(X)	0

(X) Not applicable. (D) Withheld to avoid disclosing individual company data.

3.7 Future Inorganic Chemicals Industry Developments

As a whole the inorganic chemicals industry is a basic and an expanding industry. Future changes in the industry will probably be dictated by economic and environmental considerations along with availability of raw materials. Some of the presently known probable occurrences will be:

SIC 2812: Three trends are taking place in the chlor-alkali industry that will greatly reduce the generation of hazardous wastes to land disposal: No new construction of mercury cell chlor-alkali plants, carbon anodes will be gradually replaced with coated metal anodes which will reduce the chlorinated hydrocarbon wastes in this industry, the eventual use of synthetic separators to replace asbestos separators and therefore the asbestos waste.(64) (65) (66) (67) No new Solvay Process soda ash plants are expected to be constructed in the near future because of both economic and environmental considerations.

SIC 2813: No significant changes are projected for this industry other than general growth with the national economy.

SIC 2816: Based on opinions expressed by industry members, the major trends for the inorganic pigments industries are as follows. No new sulfate process titania plants are planned for the near future and the chloride process for producing titania is expected to bear the projected expansion in the industry.(70) The chrome pigments industry is expected to experience only slow growth over the next decade.

SIC 2819: Industry opinion is that these commodities in general will experience growth in line with the national economy. Some process changes may be made or product lines dropped if certain raw materials do not become more available. A case in point is metallic zinc. One manufacturer in the Northwest is known to have closed down their zinc sulfate production because of inability to obtain zinc raw material. Otherwise, no major changes are expected in these industries.

Details and discussions of these trends are given in the Section 5 presentation for the various commodities.

4.0 INDUSTRY CHARACTERIZATION

4.1 Categorization of the Industry

The first phase of this assessment of hazardous waste practices for the Inorganic Chemicals Industry consisted of a statistical characterization of the industry in terms of the number and location of manufacturing plants, the distribution of plant sizes in terms of production capacity, the distribution of plant ages, the distribution of processes used and the distribution of actual production for each industry subcategory. The data are meant to be representative of 1974. The sources of the data are given in Section 1.1, Methodology. The data base represents a variety of time periods and was made base consistent by extrapolation.

This report covers the products manufactured in the following four major categories: (5) (6) (7) (8) (71)

SIC 2812 - Alkalies and Chlorine
SIC 2813 - Industrial Gases
SIC 2816 - Inorganic Pigments
SIC 2819 - Industrial Inorganic Chemicals (not elsewhere classified)

A further breakdown into five-digit SIC classifications is sufficiently detailed for a thorough subcategorization of the industry as follows: (5) (6) (7) (8)

SIC 2812	Alkalies and Chlorine	
	28121	Chlorine
	28122	Sodium Carbonate (Synthetic Soda Ash & Sodium Bicarbonate)
	28123	Sodium Hydroxide
	28124	Other Alkalies (includes KOH, K_2CO_3)
SIC 2813	Industrial Gases	
	28132	Acetylene
	28133	Carbon Dioxide
	28134	Elemental Gases & Other Industrial Gases (NEC) (includes A, He, H_2, N_2, O_2, N_2O, Ne)

SIC 2816 Inorganic Pigments

28161	Titanium Pigments
28162	Other White Opaque Pigments (includes White Lead, ZnO, Sb_2O_3, Lithopone, ZnS, $PbSO_4$)
28163	Chrome Colors and Other Inorganic Pigments (NEC) (includes chrome colors, white extender pigments, iron oxide pigments, colored Pb pigments, iron blues, carbon blacks)

SIC 2819 Industrial Inorganic Chemicals

28193	Sulfuric Acid (includes oleum)
28194	Inorganic Acids, except nitric and sulfuric (includes boric, chromic, HCl, HCN, HF, mixed)
28195	Aluminum Oxide
28196	Other Aluminum Compounds
28197	Potassium and Sodium Compounds (except bleaches, alkalies, and alums)
28198	Chemical Catalytic Preparations
28199	Other Inorganic Chemicals (NEC)

It should be noted that the total number of facilities making the products in the SIC 281 group that were found in this search is approximately 1,600, when broken down by this 5-digit SIC code method. This method double accounts for certain complexes making more than one of the SIC 281 commodities, as well as including plants within complexes which are not engaged primarily in 281 manufacture; e.g., chlorine plants within paper mills. Therefore the number of facilities in the 4 digit code major categories generally is less than the total of the plants in the constituent 5-digit subcategories.

In the industry characterization data tables that follow, the values given for annual production have been expressed in a form that gives no more than two significant figures so that no greater accuracy is implied than is justified by the estimation processes used to develop the values. Because of the rounding off to two significant figures, the values given for the national and regional totals will not necessarily be identical to the numerical sum of the state values.

4.2 Characterization of SIC 2812, Alkalies and Chlorine Industry

Tables 4-1 through 4-5 characterize this industry with the following information:

Table 4-1. SIC 2812 Alkalies and Chlorine, Distribution of Establishments

Number of Establishments	28121 Chlorine	28122 Synthetic Sodium Carbonates	28123 Sodium Hydroxide	28124 Other Alkalies	2812 as a Whole
IV Alabama	4		4	2	4
X Alaska					
IX Arizona					
VI Arkansas					
IX California	1		1		1
VIII Colorado					
I Connecticut					
III Delaware	1		1	1	1
IV Florida					
IV Georgia	3		3		3
IX Hawaii					
X Idaho					
V Illinois	1		1	1	1
V Indiana					
VII Iowa					
VII Kansas	1		1		1
IV Kentucky	2		2	1	2
VI Louisiana	9	2	9		10
I Maine	1		1		1
III Maryland					
I Massachusetts					
V Michigan	4	1	4	1	4
V Minnesota					
IV Mississippi	1				1
VII Missouri					
VIII Montana					
VII Nebraska					
IX Nevada	1		1		1
I New Hampshire					
II New Jersey	2		2	1	3
VI New Mexico					
II New York	5	1	2	3	5
IV North Carolina	2		2	1	3
VIII North Dakota					
V Ohio	4	2	3	1	4
VI Oklahoma					
X Oregon	1		1		1
III Pennsylvania				1	1
I Rhode Island					
IV South Carolina					
VIII South Dakota					
IV Tennessee	3		2		3
VI Texas	11	1	9	2	12
VIII Utah	1				1
I Vermont					
III Virginia	1		1		1
X Washington	4		4		4
III West Virginia	3		3		3
V Wisconsin	2		2		2
VIII Wyoming		2			2
TOTAL	67	9	59	15	74
Region I	1		1		1
II	7	1	4	4	8
III	5		5	2	6
IV	15		13	4	16
V	11	3	10	3	11
VI	20	3	18	2	22
VII	1		1		1
VIII		2			2
IX	2		2		2
X	5		5		5

Table 4-2. SIC 2812 Alkalies and Chlorine, Distribution of Plant Sizes

Plant Size,	28121 Chlorine				28122 Synthetic Sodium Carbonates				28123 Sodium Hydroxide				28124 Other Alkalies		
Daily Capacity (metric tons)	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C
IV Alabama		1	3								4				2
X Alaska															
IX Arizona															
VI Arkansas															
IX California		1								1					
VIII Colorado															
I Connecticut															
III Delaware			1								1			1	
IV Florida															
IV Georgia		1	2							1	2				
IX Hawaii															
X Idaho															
V Illinois		1									1				1
V Indiana															
VII Iowa															
VII Kansas			1								1				
IV Kentucky			2								2				1
VI Louisiana			7	2			1	1			6	3			
I Maine			1								1				
III Maryland															
I Massachusetts															
V Michigan			4					1			4			1	
V Minnesota															
IV Mississippi			1												
VII Missouri															
VIII Montana															
VII Nebraska															
IX Nevada			1								1				
I New Hampshire															
II New Jersey			2								2			1	
VI New Mexico															
II New York			5					1			2			1	2
IV North Carolina		1	1							1	1			1	
VIII North Dakota															
V Ohio		1	3				1	1		1	2			1	
VI Oklahoma															
X Oregon			1								1				
III Pennsylvania															1
I Rhode Island															
IV South Carolina															
VIII South Dakota															
IV Tennessee			3								2				
VI Texas		1	8	2			1			1	7	1		1	1
VIII Utah															
I Vermont															
III Virginia		1								1					
X Washington			4								4				
III West Virginia			3								3				
V Wisconsin			1							1	1				
VIII Wyoming							1	1							
TOTAL	0	8	54	4	0	0	4	5	0	7	46	4	0	7	8
Region I			1								1				
II			7					1			4			2	2
III		1	4							1	4			1	1
IV		3	12							2	11			1	3
V		2	8				1	2		2	8			2	1
VI		1	15	4			2	1		1	13	4		1	1
VII			1								1				
VIII							1	1							
IX		1	1							1	1				
X			5								5				

KEY: A = 0-9 metric tons; B = 10-99 metric tons; C = 100-999 metric tons; D = 1000 & over

Figure 4-3. SIC 2812 Alkalies and Chlorine, Distribution of Plant Ages

	28121 Chlorine			28122 Synthetic Sodium Carbonate			28123 Sodium Hydroxide			28124 Other Alkalies		
Plant Age (years)	A	B	C	A	B	C	A	B	C	A	B	C
IV Alabama		4						4		1	1	
X Alaska												
IX Arizona												
VI Arkansas												
IX California			1			1						
VIII Colorado												
I Connecticut												
III Delaware		1						1			1	
IV Florida												
IV Georgia		3						3				
IX Hawaii												
X Idaho												
V Illinois		1						1				1
V Indiana												
VII Iowa												
VII Kansas		1						1				
IV Kentucky		2						2			1	
VI Louisiana	2	5	2			2	2	5	2			
I Maine		1						1				
III Maryland												
I Massachusetts												
V Michigan		2	2			1		2	2			1
V Minnesota												
IV Mississippi		1										
VII Missouri												
VIII Montana												
VII Nebraska												
IX Nevada			1						1			
I New Hampshire												
II New Jersey		2						2			1	
VI New Mexico												
II New York	1	1	3			1		1	1	1	1	1
IV North Carolina		1	1					1	1		1	
VIII North Dakota												
V Ohio		3	1			2		2	1			1
VI Oklahoma												
X Oregon		1						1				
III Pennsylvania											1	
I Rhode Island												
IV South Carolina												
VIII South Dakota												
IV Tennessee	1	2				1	1					
VI Texas	3	4	4			1		5	4			
VIII Utah												2
I Vermont												
III Virginia			1						1			
X Washington		2	2					2	2			
III West Virginia	1	1	1				1	1	1			
V Wisconsin		2						2				
VIII Wyoming					2							
TOTAL	8	40	19	0	2	7	4	38	17	2	7	6
Region I		1						1				
II	1	3	3			1			1	1	2	1
III	1	2	2				1	2	2		2	
IV	1	13	1				1	11	1	1	3	
V		8	3			3		7	3			3
VI	5	9	6			3	2	10	6			2
VII		1						1				
VIII					2							
IX			2						2			
X		3	2					3	2			

KEY: A = less than 5; B = 5 to 30; C = Over 30

Table 4-4. SIC 2812 Alkalies and Chlorine, Distribution of Processes

Process Types, No. of Facilities	28121 Chlorine					28122 Synetheic Sodium Carbonate		28123 Sodium Hydroxide			28124 Other Alkalies			
	A	B	C	D	E	F	G	A	B	C	A	B	H	I
IV Alabama	4							4			2			
X Alaska														
IX Arizona														
VI Arkansas														
IX California		1							1					
VIII Colorado														
I Connecticut														
III Delaware	1							1			1			
IV Florida														
IV Georgia	2	1						2	1					
IX Hawaii														
X Idaho														
V Illinois	1							1			1			
V Indiana														
VII Iowa														
VII Kansas		1							1					
IV Kentucky	2							2			1			
VI Louisiana	3	7	1			2		3	7	1				
I Maine	1							1						
III Maryland														
I Massachusetts														
V Michigan		4				1	1		4				1	
V Minnesota														
IV Mississippi					1									
VII Missouri														
VIII Montana														
VII Nebraska														
IX Nevada		1							1					
I New Hampshire														
II New Jersey	1	1						1	1		1			
VI New Mexico														
II New York	3	2	1			1	1	1	1		1	1	1	1
IV North Carolina	1	1						1	2					1
VIII North Dakota														
V Ohio	1	2	1			2	1	1	2					1
VI Oklahoma														
X Oregon		1							1					
III Pennsylvania											1		1	
I Rhode Island														
IV South Carolina														
VIII South Dakota														
IV Tennessee	1	1	1					1	1					
VI Texas	2	8	1	2		1		2	8		1	1		
VIII Utah														
I Vermont														
III Virginia		1							1					
X Washington	2	2						2	2					
III West Virginia	2	2						2	2					
V Wisconsin								1	1					
VIII Wyoming							2							
TOTAL	28	37	5	2	1	7	5	26	37	1	9	2	4	3
Region I	1							1						
II	4	3	1			1	1	2	2		2	1	1	1
III	3	3						3	3		2		1	
IV	10	3	1		1			10	4		3		1	1
V	3	7	1			3	2	3	7		1		1	1
VI	5	15	2	2		3		5	15	1	1	1		
VII		1							1					
VIII							2							
IX		2							2					
X	2	3						2	3					

A = Mercury Cell; B = Diaphragm Cell; C = Down's Cell; D = HCl Process;
E = NOCl Process; F = Solvay Process; G = Bicarbonate Process;
H = Potassium Carbonate Process; I = Ammonium Carbonate Process

Table 4-5. SIC 2812 Alkalies and Chlorine, Distribution of Production

Annual Production 10^3 metric tons		28121 Chlorine	28122 Synthetic Sodium Carbonates	28123 Sodium Hydroxide	28124 Other Alkalies	2812 as a Whole
IV	Alabama	320		345	100	760
X	Alaska					
IX	Arizona					
VI	Arkansas					
IX	California	15		17		32
VIII	Colorado					
I	Connecticut					
III	Delaware	130		150	25	300
IV	Florida					
IV	Georgia	180		190		370
IX	Hawaii					
X	Idaho					
V	Illinois	32		59	55	150
V	Indiana					
VII	Iowa					
VII	Kansas	73		80		150
IV	Kentucky	200		220	23	440
VI	Louisiana	2,600	960	2,700		6,300
I	Maine	65		72		140
III	Maryland					
I	Massachusetts					
V	Michigan	510	750	560		1,800
V	Minnesota					
IV	Mississippi	46				46
VII	Missouri					
VIII	Montana					
VII	Nebraska					
IX	Nevada	48		53		100
I	New Hampshire					
II	New Jersey	240		260	0	500
VI	New Mexico					
II	New York	460	1,000	140	9	1,600
IV	North Carolina	71		78	0	150
VIII	North Dakota					
V	Ohio	260	790	250	30	1,300
VI	Oklahoma					
X	Oregon	130		110		240
III	Pennsylvania				0	0
I	Rhode Island					
IV	South Carolina					
VIII	South Dakota					
IV	Tennessee	330		290		620
VI	Texas	4,000	270	2,000	6.6	6,300
VIII	Utah	73				73
I	Vermont					
III	Virginia	17		18		35
X	Washington	330		310		600
III	West Virginia	590		650		1,200
V	Wisconsin	76		88		160
VIII	Wyoming		640			640
TOTAL		11,000	4,400	8,600	250	24,000
Region I		65		72		140
II		700	1,000	400	9	2,100
III		740		820	25	1,500
IV		1,100		1,100	120	2,400
V		880	1,500	960	85	3,400
VI		6,600	1,200	4,700	6.6	13,000
VII		73		80		150
VIII		73	640			700
IX		63		70		130
X		460		420		840

Table 4-1 gives the distribution and number of establishments producing the products in the four 5-digit SIC subcategories. The number of establishments covered in SIC 2812 was 78 with the heaviest concentration in EPA Region VI (almost 30%). Louisiana and Texas contain all of the Region VI SIC 2812 facilities.

Table 4-2 gives the distribution of plant sizes by daily production capacity in the four industry subcategories. Seventy-six percent of SIC 28121 plants have daily capacities in the range of 100-999 tons. SIC 28122 plants are divided 44 percent in the 100-999 tons per day range and 56 percent in the over 1000 tons per day class. Most (81 percent) SIC 28123 plants are in the 100-999 tons per day range. The other alkalies subcategory, SIC 28124, is almost evenly divided into the 10-99 tons per day and 100-999 tons per day brackets.

Table 4-3 lists the distribution of plant ages in SIC 2812. Most SIC 28121 and SIC 28123 plants (approximately 60%) fall in the 5-30 year age range. Over 75% of SIC 28122 plants are over 30 years old and over 85% of SIC 28124 plants are almost evenly split in the two age ranges of 5-30 years and over 30 years. The reason for the relatively old distribution of ages in 28122 is the lack of new construction of Solvay plants because of the recent exploitation of natural sources of soda ash.

Table 4-4 shows the distribution by process types in SIC 2812.

Table 4-5 lists the distribution of production in this industry. About 54% of total production in SIC 2812 takes place in EPA Region VI.

According to the 1972 Census of Manufacturers, the establishments primarily engaged in SIC 2812 manufacture average 283 total employees per establishment and 202 production employees per establishment. Eighty-one percent of the reported establishments have 20 or more employees.

4.3 Characterization of SIC 2813, Industrial Gases Industry

Tables 4-6 through 4-10 characterize this industry with the following information:

Table 4-6 gives the distribution and number of establishments producing the products in the three 5-digit SIC subcategories. The number of establishments covered in

Table 4-6. SIC 2813 Industrial Gases, Distribution of Establishments

Number of Establishments	28132 Acetylene	28133 Carbon Dioxide	28134 Other Industrical Gases	2813 as a Whole
IV Alabama	3	2	11	13
X Alaska	2	1	2	3
IX Arizona	2		4	5
VI Arkansas	1	2	1	3
IX California	6	9	40	47
VIII Colorado	4	1	4	5
I Connecticut	1		3	3
III Delaware		1	6	7
IV Florida	6	2	8	13
IV Georgia	3	3	6	10
IX Hawaii	2	2	4	6
X Idaho	2		2	2
V Illinois	4	3	16	20
V Indiana	4	1	7	9
VII Iowa	2	6	3	9
VII Kansas	2	5	11	17
IV Kentucky	2	1	3	5
VI Louisiana	7	10	20	31
I Maine	1		1	1
III Maryland	2		2	3
I Massachusetts	2	2	5	7
V Michigan	2		7	8
V Minnesota	3		5	6
IV Mississippi	3	1	2	5
VII Missouri	3	2	6	9
VIII Montana	2		3	3
VII Nebraska	1	3		4
IX Nevada	1		2	3
I New Hampshire				
II New Jersey	2	1	18	18
VI New Mexico	1	2	1	3
II New York	3	1	9	10
IV North Carolina	2	2	2	5
VIII North Dakota				
V Ohio	6	9	28	40
VI Oklahoma	3	3	7	11
X Oregon	2	1	3	4
III Pennsylvania	8	4	28	33
I Rhode Island				
IV South Carolina	1		1	2
VIII South Dakota	1			1
IV Tennessee	6	4	9	17
VI Texas	17	20	46	69
VIII Utah	1	2	3	5
I Vermont				
III Virginia	3	3	7	12
X Washington	2	3	3	7
III West Virginia	3	2	13	15
V Wisconsin	2		2	2
VIII Wyoming	1	2	1	3
TOTAL	137	116	365	514
Region I	4	2	9	11
II	5	2	27	28
III	16	10	56	70
IV	26	15	42	70
V	21	13	65	85
VI	29	37	75	117
VII	8	16	20	39
VIII	9	5	11	17
IX	11	11	50	61
X	8	5	10	16

Table 4-7. SIC 2813 Industrial Gases, Distribution of Plant Sizes

Plant Size	28132 Acetylene			28133 Carbon Dioxide				28134 Other Industrial Gases			
Daily Capacity (metric tons)	A	B	C	A	B	C	D	A	B	C	D
IV Alabama		2	1		1	1				10	1
X Alaska	2						1		1	1	
IX Arizona	1	1							3	1	
VI Arkansas			1			2				1	
IX California	1	5			2	7		2	5	30	3
VIII Colorado		4			1				2	2	
I Connecticut	1							1	1	1	
III Delaware						1		2	1	3	
IV Florida	1	4	1		1	1		1	4	3	
IV Georgia		3				3			3	3	
IX Hawaii	2			1	1				2	2	
X Idaho		2							2		
V Illinois	3	1				3		3	2	8	3
V Indiana	3	1			1			1		3	3
VII Iowa	1	1			1	5			1	2	
VII Kansas		2			1	4			10	1	
IV Kentucky			2			1		1	1	1	
VI Louisiana		6	1		2	6	2		3	13	4
I Maine	1								1		
III Maryland		2							1		1
I Massachusetts	2				1	1			3	2	
V Michigan	2					1			1	5	1
V Minnesota	2	1							2	3	
IV Mississippi		3								2	
VII Missouri						2			2	3	1
VIII Montana		2							2	1	
VII Nebraska	1				1	2					
IX Nevada		1							1	1	
I New Hampshire											
II New Jersey	1	1				1		3	8	5	2
VI New Mexico		1			2				1		
II New York	2	1				1			2	4	3
IV North Carolina		2			1	1				2	
VIII North Dakota											
V Ohio		5	1		1	7	1	3	5	14	6
VI Oklahoma		3			2	1		2	2	3	
X Oregon	2					1		1	1	1	
III Pennsylvania	7	1				4		2	4	18	4
I Rhode Island											
IV South Carolina		1									1
VIII South Dakota		1									
IV Tennessee	1	4	1			4			2	6	1
VI Texas	2	13	2	1	4	10	5	2	9	27	8
VIII Utah		1		1	1					3	
I Vermont											
III Virginia	1	2				3			3	4	
X Washington		2			1	2			2	1	
III West Virginia	1	2				2		1	1	6	5
V Wisconsin	2									1	1
VIII Wyoming	1					2				1	
TOTAL	46	81	10	3	25	79	9	25	94	198	48
Region I	4				1	1		1	5	3	
II	3	2				2		3	12	9	5
III	9	7				10		5	10	31	10
IV	2	19	5		3	12		2	10	27	3
V	12	8	1		2	10	1	7	10	34	14
VI	2	23	4	1	10	19	7	4	15	44	12
VII	5	3			3	13			12	7	1
VIII	1	8		1	2	2			5	6	
IX	4	7		1	3	7		2	11	34	3
X	4	4			1	3	1	1	6	3	

KEY: A = 0-9 metric tons; B = 10-99 metric tons; C = 100-999 metric tons; D = 1000 & up

Table 4-8. SIC 2813 Industrial Gases, Distribution of Plant Ages

		28132 Acetylene			28133 Carbon Dioxide			28134 Other Industrial Gases		
Plant Age (years)		A	B	C	A	B	C	A	B	C
IV	Alabama	1	2			2		1	8	2
X	Alaska		2			1			2	
IX	Arizona	1	1					1	2	1
VI	Arkansas		1		1	1			1	
IX	California	2	4		3	5	1	10	22	8
VIII	Colorado		4			1		1	3	
I	Connecticut		1					1	2	
III	Delaware					1		1	5	
IV	Florida	1	4	1		2		2	5	1
IV	Georgia		2	1	1	2		1	4	1
IX	Hawaii		2			2		1	2	1
X	Idaho		2						2	
V	Illinois		3	1	1	2		3	11	2
V	Indiana	1	2	1		1		1	6	
VII	Iowa		2		2	3	1	1	2	
VII	Kansas	1	1		1	4		2	9	
IV	Kentucky			2		1			3	
VI	Louisiana	1	4	2	3	6	1	4	14	2
I	Maine		1						1	
III	Maryland		2						2	
I	Massachusetts		2			2		1	4	
V	Michigan		2					2	4	1
V	Minnesota	1	2					1	4	
IV	Mississippi		2	1		1			2	
VII	Missouri		3			2		1	5	
VIII	Montana		2					1	2	
VII	Nebraska		1		1	2				
IX	Nevada		1						2	
I	New Hampshire									
II	New Jersey		2			1		3	13	2
VI	New Mexico		1			2			1	
II	New York		2	1		1		3	5	1
IV	North Carolina		2		1	1			2	
VIII	North Dakota									
V	Ohio	1	4	1	2	6	1	5	20	3
VI	Oklahoma		3		1	2		2	5	
X	Oregon		2			1			3	
III	Pennsylvania	1	6	1	1	3		5	20	3
I	Rhode Island									
IV	South Carolina		1						1	
VIII	South Dakota		1							
IV	Tennessee	1	5		1	3		2	6	1
VI	Texas	2	13	2	6	12	2	9	34	3
VIII	Utah		1		1	1		1	2	
I	Vermont									
III	Virginia		3			3		1	5	1
X	Washington		2			3		1	2	
III	West Virginia		3			2		3	10	
V	Wisconsin		2						2	
VIII	Wyoming		1			2			1	
TOTAL		14	109	14	26	84	6	71	261	33
Region I			4			2		2	7	
II			4	1		2		6	18	3
III		1	14	1	1	9		10	42	4
IV		3	18	5	3	12		6	31	5
V		3	15	3	3	9	1	12	47	6
VI		3	22	4	11	23	3	15	55	5
VII		1	7		4	11	1	4	16	
VIII			9		1	4		3	8	
IX		3	8		3	7	1	12	28	10
X			8			5		1	9	

KEY: A = Under 5; B = 5 to 30; C = Over 30

Table 4-9. SIC 2813 Industrial Gases, Distribution of Processes

Process Type, No. of Facilities	28132 Acetylene (from carbide)	28133 Carbon Dioxide			28134 Other Industrial Gases			
		A	B	C	D	E	F	G
IV Alabama	3	2			7	4		
X Alaska	2	1			2			
IX Arizona	2				3	2		1
VI Arkansas	1		2		1			
IX California	6	7	1	1	24	23	2	2
VIII Colorado	4		1		4	2		1
I Connecticut	1				2	1		1
III Delaware				1	2	5		
IV Florida	6	2			7	3		
IV Georgia	3	3			4	3		
IX Hawaii	2	2			2	3		
X Idaho	2				2			
V Illinois	4	3			11	9		
V Indiana	4	1			5	3		1
VII Iowa	2	6			3			
VII Kansas	2	3	1	1	1	3	1	6
IV Kentucky	2			1	2	3		
VI Louisiana	7	8	2		13	9		
I Maine	1				1			
III Maryland	2				2			
I Massachusetts	2	2			5	2		1
V Michigan	2				5	2		
V Minnesota	3				4	1		
IV Mississippi	3	1			2			
VII Missouri	3	2			6			
VIII Montana	2				3			
VII Nebraska	1	3						
IX Nevada	1					1		1
I New Hampshire								
II New Jersey	2	1			8	10	1	1
VI New Mexico	1			2	1			
II New York	3	1			8	3		1
IV North Carolina	2	2			2			
VIII North Dakota								
V Ohio	6	8		1	18	11	1	
VI Oklahoma	3	2		1	5			2
X Oregon	2	1			2	2		
III Pennsylvania	8	2		2	25	8		1
I Rhode Island								
IV South Carolina	1				1			
VIII South Dakota	1							
IV Tennessee	6	3	1		6	6		1
VI Texas	17	12	6	2	26	21	1	5
VIII Utah	1	1	1		3			
I Vermont								
III Virginia	3	2	1		6	1	1	1
X Washington	2	3			3			
III West Virginia	3	2			6	5		
V Wisconsin	2				2			
VIII Wyoming	1	1	1		1			
TOTAL	137	87	18	11	246	146	7	26
Region I	6	2			8	3		2
II	2	2			16	13	1	2
III	5	6	1	3	41	19	1	2
IV	8	13	1	1	31	13		1
V	6	12		1	45	32	1	1
VI	5	22	11	4	46	30	1	7
VII	4	14	1	1	10	3	1	6
VIII	6	2	3		11	2		1
IX	4	9	1	1	29	29	2	4
X	4	5			9	2		

KEY: A = NH_3 by-product; B = Natural Gas Wells; C = Other; D = Air Separation; E = CO and H_2 process; F = Nitrous Oxide; G = Helium

Table 4-10. SIC 2813 Industrial Gases, Distribution of Production

Annual Production 10^3 metric tons		28132 Acetylene	28133 Carbon Dioxide	28134 Other Industrial Gases	2813 as a Whole
IV	Alabama	15	9	500	520
X	Alaska	1	5	18	24
IX	Arizona	2		75	77
VI	Arkansas	7	41	160	210
IX	California	5	110	1,200	1,300
VIII	Colorado	8	17	82	110
I	Connecticut	1		11	12
III	Delaware		28	200	230
IV	Florida	30	85	120	230
IV	Georgia	15	18	140	170
IX	Hawaii	1	51	44	96
X	Idaho	4		36	40
V	Illinois	3	44	1,900	1,900
V	Indiana	3	43	830	880
VII	Iowa	2	95	55	150
VII	Kansas	3	47	78	130
IV	Kentucky	7	28	280	310
VI	Louisiana	30	105	970	1,100
I	Maine	1		13	14
III	Maryland	7		220	230
I	Massachusetts	2	17	100	120
V	Michigan	4		950	950
V	Minnesota	2		190	190
IV	Mississippi	4	28	84	120
VII	Missouri	1	9	260	270
VIII	Montana	5		37	42
VII	Nebraska	1	14		15
IX	Nevada	2		4	6
I	New Hampshire				
II	New Jersey	2	17	400	420
VI	New Mexico	4	17	1	22
II	New York	3	35	580	620
IV	North Carolina	15	28	170	210
VIII	North Dakota				
V	Ohio	6	130	1,900	2,000
VI	Oklahoma	11	62	5	78
X	Oregon	2	5	25	32
III	Pennsylvania	5	17	3,300	3,300
I	Rhode Island				
IV	South Carolina	4		160	160
VIII	South Dakota	2			2
IV	Tennessee	30	57	440	530
VI	Texas	110	180	3,800	4,100
VIII	Utah	5	17	150	170
I	Vermont				
III	Virginia	15	28	230	270
X	Washington	3	34	55	92
III	West Virginia	15	28	1,200	1,200
V	Wisconsin	2	43	300	340
VIII	Wyoming	1	9	5	15
TOTAL		400	1,500	21,000	23,000
Region I		2	17	120	150
II		7	52	980	1,000
III		42	100	5,100	5,200
IV		120	250	1,900	2,200
V		20	260	6,100	6,300
VI		160	400	4,900	5,500
VII		7	160	390	560
VIII		21	43	270	340
IX		10	160	1,300	1,500
X		10	44	130	190

SIC 2813 was 514 with over 65% of them located in EPA Regions III, IV, V and VI.

Table 4-7 gives the distribution of plant sizes by daily production capacity in the three industry subcategories. Fifty-nine percent of SIC 28132 plants have daily capacities in the range of 10-99 tons. Sixty-eight percent of SIC 28133 plants fall into the 100-999 tons per day range and the majority (54%) of SIC 28134 plants fall into the same range.

Table 4-8 lists the distribution of plants ages in SIC 2813. Most of the plants in this industry fall into the 5-30 year age bracket: 80% in SIC 28132, 72% in SIC 28133 and 71% in SIC 28134.

Table 4-9 shows the distribution by process types in SIC 2813. Acetylene is made by only one process in SIC 281 facilities. The bulk of carbon dioxide plants (75%) use the ammonia by-product process. The vast majority of SIC 28134 plants use either air separation or carbon monoxide/hydrogen processes.

Table 4-10 lists the distribution of production in this industry. The industry as a whole produces about 23,000,000 metric tons per year of products with the heaviest output being in EPA Regions III, V and VI.

According to the 1972 Census of Manufacturers, the establishments primarily engaged in SIC 2813 manufacture average 19 total employees per establishment and 11 production employees per establishment. Only 27 percent of the reported establishments have 20 or more employees.

4.4 Characterization of SIC 2816, Inorganic Pigments Industry

Tables 4-11 through 4-15 characterize this industry with the following information:

Table 4-11 gives the distribution and number of establishments producing the products in the three 5-digit SIC subcategories. The number of establishments covered in SIC 2816 was 92 with the heaviest concentrations (66% of total) in EPA Regions II, III and V.

Table 4-12 gives the distribution of plant sizes by daily production capacity in the three industry subcategories. Seventy-three percent of SIC 28161 plants have daily capacities in the range of 100-999 tons. Both SIC 28162 and

Table 4-11. SIC 2816 Inorganic Pigments, Distribution of Establishments

Number of Establishments	28161 Titanium Pigments	28162 Other White Opaque Pigments	28163 Chrome Colors and Other Pigments	2816 as a Whole
IV Alabama				
X Alaska				
IX Arizona				
VI Arkansas				
IX California	1	3	4	8
VIII Colorado			1	1
I Connecticut				
III Delaware	1			1
IV Florida				
IV Georgia	1	2	2	5
IX Hawaii				
X Idaho		1		1
V Illinois		5	4	9
V Indiana		1	3	4
VII Iowa				
VII Kansas		2		2
IV Kentucky			1	1
VI Louisiana				
I Maine				
III Maryland	1	2	2	5
I Massachusetts				
V Michigan		1		1
V Minnesota				
IV Mississippi	1		1	2
VII Missouri	1		3	4
VIII Montana		2		2
VII Nebraska				
IX Nevada			1	1
I New Hampshire				
II New Jersey	2	4	10	16
VI New Mexico				
II New York		1	4	5
IV North Carolina				
VIII North Dakota				
V Ohio	2	2	3	7
VI Oklahoma				
X Oregon				
III Pennsylvania		3	7	10
I Rhode Island				
IV South Carolina				
VIII South Dakota				
IV Tennessee	1			1
VI Texas		1	1	2
VIII Utah				
I Vermont				
III Virginia			1	1
X Washington			1	1
III West Virginia			2	2
V Wisconsin				
VIII Wyoming				
TOTAL	11	30	51	92
Region I				
II	2	5	14	21
III	2	5	12	19
IV	3	2	4	9
V	2	9	10	21
VI		1	1	2
VII	1	2	3	6
VIII		2	1	3
IX	1	3	5	9
X		1	1	2

Table 4-12. SIC 2816 Inorganic Pigments, Distribution of Plant Sizes

Plant Size, Daily Capacity (metric tons)	28161 Titanium Pigments			28162 Other White Opaque Pigments			28163 Chrome Colors and Other Pigments		
	A	B	C	A	B	C	A	B	C
IV Alabama									
X Alaska									
IX Arizona									
VI Arkansas									
IX California		1		2	1		2	2	
VIII Colorado								1	
I Connecticut									
III Delaware			1						
IV Florida									
IV Georgia			1		2			2	
IX Hawaii									
X Idaho					1				
V Illinois				1	4		1	3	
V Indiana					1		1	2	
VII Iowa									
VII Kansas					2				
IV Kentucky								1	
VI Louisiana									
I Maine									
III Maryland			1	1	1			1	1
I Massachusetts									
V Michigan					1				
V Minnesota									
IV Mississippi			1				1		
VII Missouri			1				1	2	
VIII Montana					2				
VII Nebraska									
IX Nevada								1	
I New Hampshire									
II New Jersey			2	1	3		3	6	1
VI New Mexico									
II New York					1		1	3	
IV North Carolina									
VIII North Dakota									
V Ohio		2		1	1		1	2	
VI Oklahoma									
X Oregon									
III Pennsylvania					2	1	2	4	1
I Rhode Island									
IV South Carolina									
VIII South Dakota									
IV Tennessee			1						
VI Texas					1			1	
VIII Utah									
I Vermont									
III Virginia								1	
X Washington								1	
III West Virginia								2	
V Wisconsin									
VIII Wyoming									
TOTAL	0	3	8	6	23	1	13	35	3
Region I									
II			2	1	4		4	9	1
III			2	1	3	1	2	8	2
IV			3		2		1	3	
V		2		2	7		3	7	
VI					1			1	
VII			1		2		1	2	
VIII					2			1	
IX		1		2	1		1	3	
X					1			1	

KEY: A = 0-9 metric tons; B = 10-99 metric tons; C = 100-999 metric tons;
D = 1000 & Over

Table 4-13. SIC 2816 Inorganic Pigments, Distribution of Plant Ages

		28161 Titanium Pigments			28162 White and Opaque Pigments			28163 Chrome Colors and Other Pigments		
Plant Age (years)		A	B	C	A	B	C	A	B	C
IV	Alabama									
X	Alaska									
IX	Arizona									
VI	Arkansas									
IX	California		1		1	1	1	1	2	1
VIII	Colorado								1	
I	Connecticut									
III	Delaware			1						
IV	Florida									
IV	Georgia		1		1	1			1	1
IX	Hawaii									
X	Idaho					1				
V	Illinois				1	3	1		2	2
V	Indiana					1		1	1	1
VII	Iowa									
VII	Kansas						2			
IV	Kentucky									1
VI	Louisiana									
I	Maine									
III	Maryland		1			2			1	1
I	Massachusetts									
V	Michigan					1				
V	Minnesota									
IV	Mississippi		1						1	
VII	Missouri			1					2	1
VIII	Montana				1	1				
VII	Nebraska									
IX	Nevada								1	
I	New Hampshire									
II	New Jersey		1	1	1	2	1	2	4	4
VI	New Mexico									
II	New York					1			3	1
IV	North Carolina									
VII	North Dakota									
V	Ohio		2			1	1	1	1	1
VI	Oklahoma									
X	Oregon									
III	Pennsylvania					1	2	1	3	3
I	Rhode Island									
IV	South Carolina									
VIII	South Dakota									
IV	Tennessee		1							
VI	Texas					1			1	
VIII	Utah									
I	Vermont									
III	Virginia								1	
X	Washington								1	
III	West Virginia								2	
V	Wisconsin									
VIII	Wyoming									
TOTAL			8	3	5	17	8	6	28	17
Region I										
	II		1	1	1	3	1	2	7	5
	III			1		3	2	1	7	4
	IV		3		1	1			2	2
	V		2		1	6	2	2	4	4
	VI					1			1	
	VII			1			2		2	1
	VIII				1	1			1	
	IX		1		1	1	1	1	3	1
	X					1			1	

KEY: A = less than 5; B = 5 to 30; C = Over 30

Table 4-14. SIC 2816 Inorganic Pigments, Distribution of Processes

		28161 Titanium Pigments		28162 Other White Opaque Pigments			28163 Chrome Colors and Other Pigments				
Process Type, No. of Facilities		Sulfate	Chloride	$PbSO_4$ & $PbCO_3$	Zinc Oxide	Aluminum Oxide	A	B	C	D	E
IV	Alabama										
X	Alaska										
IX	Arizona										
VI	Arkansas										
IX	California		1	1	2				1	2	1
VIII	Colorado									1	
I	Connecticut										
III	Delaware	1	1								
IV	Florida										
IV	Georgia	1	1		2					1	1
IX	Hawaii										
X	Idaho				1						
V	Illinois			1	4				3	1	
V	Indiana			1						2	1
VII	Iowa										
VII	Kansas				2						
IV	Kentucky						1				
VI	Louisiana										
I	Maine										
III	Maryland	1	1			2	1		1		1
I	Massachusetts										
V	Michigan				1						
V	Minnesota										
IV	Mississippi		1						1		
VII	Missouri	1							1	2	1
VIII	Montana				2						
VII	Nebraska										
IX	Nevada									1	
I	New Hampshire										
II	New Jersey	2		2		2	3	1	5	1	1
VI	New Mexico										
II	New York			1	1		2	2	1	1	2
IV	North Carolina										
VIII	North Dakota										
V	Ohio		2		1	1	1	1			2
VI	Oklahoma										
X	Oregon										
III	Pennsylvania				3		1		4	1	3
I	Rhode Island										
IV	South Carolina										
VIII	South Dakota										
IV	Tennessee		1								
VI	Texas					1				1	
VIII	Utah										
I	Vermont										
III	Virginia								1		
X	Washington									1	
III	West Virginia						1	1		1	
V	Wisconsin										
VIII	Wyoming										
TOTAL		6	8	6	19	6	10	5	18	16	13
Region I											
II		2		3	1	2	5	3	6	2	3
III		2	2		3	2	3	1	6	2	4
IV		1	3		2		1		1	1	1
V			2	2	6	1	1	1	3	3	3
VI						1				1	
VII		1			2				1	2	1
VIII					2					1	
IX			1	1	2				1	3	1
X					1					1	

KEY: A = Chrome Pigments; B = Iron Blues; C = Iron Oxide; D = Lead Oxide; E = Others

Table 4-15. SIC 2816 Inorganic Pigments, Distribution of Production

Annual Production 10^3 metric tons		28161 Titanium Pigments	28162 Other White Opaque Pigments	28163 Chrome Colors and Other Pigments	2816 as a Whole
IV	Alabama				
X	Alaska				
IX	Arizona				
VI	Arkansas				
IX	California	22	8	53	83
VIII	Colorado			0.5	0.5
I	Connecticut				
III	Delaware	94			94
IV	Florida				
IV	Georgia	94	4.7	25	120
IX	Hawaii		31		31
X	Idaho		32	35	67
V	Illinois		3.8	7.5	11
V	Indiana				
VII	Iowa		51		51
VII	Kansas			3	3
IV	Kentucky				
VI	Louisiana				
I	Maine				
III	Maryland	66	0.6	25	92
I	Massachusetts				
V	Michigan		2.9		2.9
V	Minnesota				
IV	Mississippi	37		4	41
VII	Missouri	90		65	150
VIII	Montana		5		5
VII	Nebraska				
IX	Nevada			3	3
I	New Hampshire				
II	New Jersey	134	23	52	210
VI	New Mexico				
II	New York		3	31	34
IV	North Carolina				
VIII	North Dakota				
V	Ohio	45	9	5.3	59
VI	Oklahoma				
X	Oregon				
III	Pennsylvania		80	94	170
I	Rhode Island				
IV	South Carolina				
VIII	South Dakota				
IV	Tennessee	120			120
VI	Texas		0.4	20	20
VIII	Utah				
I	Vermont				
III	Virginia			4	4
X	Washington			2	2
III	West Virginia			27	27
V	Wisconsin				
VIII	Wyoming				
TOTAL		700	250	460	1,400
Region I					
II		134	26	83	240
III		160	81	150	390
IV		250	4.7	32	280
V		45	48	48	140
VI			0.4	20	20
VII		90	51	65	200
VIII			5	0.5	5
IX		22	8	56	86
X			32	2	33

SIC 28163 have the majority of plants (77% for SIC 28162 and 69% for SIC 28163) in the 10-99 tons per day range.

Table 4-13 lists the distribution of plant ages in SIC 2816. Most of the plants in SIC 2816 fall into the 5-30 year age bracket: 73% in SIC 28161, 57% in SIC 28162 and 55% in SIC 28163. Twelve percent of the total number of plants in SIC 2816 are less than 5 years old.

Table 4-14 shows the distribution by process types in SIC 2816. Titania (SIC 28161) is made by two processes; sulfate and chloride. Most of the SIC 28162 plants (over 60%) are zinc oxide producers. The processes listed under SIC 28163 are fairly evenly divided among chrome pigments/iron blues, iron oxides, lead oxides and others.

Table 4-15 lists the distribution of production in this industry. The industry as a whole produces about 1,400,000 metric tons per year of products with the heaviest output being in EPA Regions II, III, IV, V and VII accounting for about 90% of the total.

According to the 1972 Census of Manufacturers, the establishments primarily engaged in SIC 2816 manufacture average 115 total employees per establishment and 81 production employees per establishment. Sixty percent of the reported establishments have 20 or more employees.

4.5 Characterization of SIC 2819, Inorganic Chemicals, N.E.C. Industry

Tables 4-16 through 4-20 characterize this industry with the following information:

Table 4-16 gives the distribution and number of establishments producing the products in the seven 5-digit SIC subcategories. The number of establishments covered in SIC 2819 was 923. EPA Region VI has the most plants, 189. The next heaviest concentrations are in EPA Regions IV and V with 156 and 140 plants, respectively. The lowest concentrations are in EPA Regions I, VIII and X with a total of 84 for all three regions. The largest number of plants are in SIC 28199 (almost 50% of the total).

Table 4-17 gives the distribution of plant sizes by daily production capacity in the seven industry subcategories. In SIC subcategories 28194, 28196, 28197 and 28199 the 10-99 tons per day range is the most frequently encountered. SIC 28193 has most of its plants in the 100-999 tons per day range (about 71%). All of SIC 28198 plants are in the 0-9 tons per day range.

Table 4-16. SIC 2819 Industrical Inorganic Chemicals, N.E.C., Distribution of Establishments

Number of Establishments	28193 Sulfuric Acid	28194 Inorganic Acids	28195 Aluminum Oxide	28196 Aluminum Compounds	28197 Na and K Compounds	28198 Chem. Catalytic Preparation	28199 Other Inorg. Chem. N.E.C.	2819 as a Whole
IV Alabama	3	2	1	6	6		9	23
X Alaska								
IX Arizona	5				2			7
VI Arkansas	6		2	3	1	1	6	14
IX California	10	11	2	9	24	11	41	85
VIII Colorado				1	1			2
I Connecticut				1				1
III Delaware	1	2		1	3		2	6
IV Florida	15	3		4	6	1	9	34
IV Georgia	4	7		6	12		7	30
IX Hawaii	1						1	2
X Idaho	3						4	7
V Illinois	13	6		5	14	3	26	48
V Indiana	4	2		2	6	2	8	17
VII Iowa	1						4	5
VII Kansas	2	1			3		5	10
IV Kentucky	2	4	1		1	2	3	8
VI Louisiana	11	10	3	9	9	1	15	40
I Maine	1			1	1		1	3
III Maryland	4	4		2	5	2	10	19
I Massachusetts	1	3	1	1	6	1	5	16
V Michigan	3	5		4	6	3	9	21
V Minnesota	1			2			2	4
IV Mississippi	1		1	3	3	1	5	11
VII Missouri	3	1		2	7	1	13	24
VIII Montana	1					1	5	6
VII Nebraska					1		1	2
IX Nevada	1	2			2		3	7
I New Hampshire								
II New Jersey	11	13	1	9	21	8	38	76
VI New Mexico	4	1			9		9	20
II New York	2	4	1	4	10	1	17	29
IV North Carolina	4	2		2	7		4	18
VIII North Dakota							2	2
V Ohio	7	10		8	12	5	23	44
VI Oklahoma	2	1		1	1		5	6
X Oregon		1		1	1	1	1	4
III Pennsylvania	8	3	1	4	15	2	24	47
I Rhode Island	1				1		1	2
IV South Carolina	1	2		2	2		3	9
VIII South Dakota								
IV Tennessee	1	4	1	6	6	1	11	23
VI Texas	17	19	2	5	14	2	75	109
VIII Utah	1		1	1	4	1	7	11
I Vermont							2	2
III Virginia	7	1		3	5	1	5	19
X Washington	3	3		5	6	1	9	20
III West Virginia	1	8			4	2	5	16
V Wisconsin				2	2		2	6
VIII Wyoming	2				1		5	8
TOTAL	169	135	18	115	240	55	442	923
Region I	3	3	1	3	8	1	9	24
II	13	17	2	13	31	9	55	105
III	21	18	1	10	32	7	46	107
IV	31	24	4	29	43	5	51	156
V	28	23		23	40	13	70	140
VI	40	31	7	18	34	4	110	189
VII	4	2		2	11	1	23	41
VIII	4		1	2	6	2	19	29
IX	17	13	2	9	28	11	45	101
X	6	4		6	7	2	14	31

Table 4-17. SIC 2819 Industrial Inorganic Chemicals, N.E.C., Distribution of Plant Sizes

Plant Size,	28193 Sulfuric Acid				28194 Inorganic Acids				28195 Aluminum Oxide				28196 Other Aluminum Compounds				28197 Na and K Compounds				28198 Chem. Catalytic Preparation		28199 Other Inorg. Chem. N.E.C.			
Daily Capacity (metric tons)	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	A	B	C	D
IV Alabama		1	2			1	1					1		4	2		1	3	2					5	4	
X Alaska																										
IX Arizona			4	1													1	1								
VI Arkansas			6								1	1			2	1		1			1			5	1	
IX California			10		1	3	7		1	1			6	3			3	12	7	2	11		9	21	11	
VIII Colorado															1			1								
I Connecticut														1												
III Delaware			1			2									1		1	2						1	1	
IV Florida		1	3	11		2	1							2	2		2	3	1		1		1	8		
IV Georgia		2	2		1	4	2						1	5			1	7	4				2	2	3	
IX Hawaii			1																					1		
X Idaho			2	1																				2	2	
V Illinois		2	9	2		2	2	2						3	2		2	6	5	1	3		5	11	10	
V Indiana			3	1		1	1							1	1			3	2	1	2		1	4	3	
VII Iowa			1																				1	2	1	
VII Kansas			2			1												2	1				1	2	2	
IV Kentucky			2			1	3											1			2			2	1	
VI Louisiana		1	4	6	1	5	3	1				3		2	6	1	1	2	6		1		2	4	5	4
I Maine			1												1			1						1		
III Maryland		1	3			2	2								2		1	3	1		2		2	5	3	
I Massachusetts			1			3					1				1		1	2	3		1		1	2	2	
V Michigan		2	1			2	3							2	2			2	3	1	3		1	2	5	1
V Minnesota			1											1	1									1	1	
IV Mississippi				1							1			1	2			1	2		1			2	1	2
VII Missouri			3			1								1	1			4	3		1		2	3	5	1
VIII Montana			1																		1			3	2	
VII Nebraska																		1						1		
IX Nevada			1			2												2					1	1	1	
I New Hampshire																										
II New Jersey		1	9	1		10	3		1				1	6	2		2	7	9	3	8		10	17	11	
VI New Mexico			4			1												2	3	4				8		
II New York		1	1		1	1	2			1			1	2	1		1	3	3	3	1		2	9	6	
IV North Carolina			3	1		1	1							2				5	2				1	2	1	
VIII North Dakota																							1		1	
V Ohio			7		1	5	4						1	5	2		3	6	3		5		5	9	9	
VI Oklahoma			2		1									1			1						2	2	1	
X Oregon						1								1				1			1			1		
III Pennsylvania		1	7		2	1				1				2	2		2	6	5	2	2		6	11	7	
I Rhode Island		1																	1					1		
IV South Carolina			1			1	1						1	1				1	1					2	1	
VIII South Dakota																										
IV Tennessee				1		1	3			1			1	3	2		1	3	2		1		1	3	7	
VI Texas		2	11	4	4	8	6	1			1	1		1	2	2	2	5	7		2		11	39	21	4
VIII Utah				1						1					1				3	1	1		1	3	3	
I Vermont																								1	1	
III Virginia		1	6		1									1	2			3	2		1			2	3	
X Washington		1	2		2	1								2	3		1	3	2		1			5	4	
III West Virginia			1			7	1											2	2		2		1	2	2	
V Wisconsin														1	1			1	1					1	1	
VIII Wyoming			2																1					5		
TOTAL		18	120	31	15	70	46	4	2	6	4	6	12	54	45	4	27	108	87	18	55	0	71	216	143	12
Region I		1	2			3					1			1	2		1	3	4		1		1	5	3	
II		2	10	1	1	11	5		1	1			2	8	3		3	10	12	6	9		12	26	17	
III		3	18		3	12	3			1				3	7		4	16	10	2	7		9	21	16	
IV		4	13	14	1	11	12			2	1	1	3	18	8		5	24	14		5		5	26	18	2
V		4	21	3	1	10	10	2					5	13	9		5	18	14	3	13		12	28	29	1
VI		3	27	10	6	14	9	2			2	5		4	10	4	4	10	16	4	4		16	58	28	8
VII			6			2								1	1			7	4		1		4	10	8	1
VIII			3	1						1					2			1	4	1	2		2	11	6	
IX			16	1	1	5	7		1	1			6	3			4	15	7	2	11		10	23	12	
X		1	4	1	2	2								3	3		1	4	2		2			8	6	

KEY: A = 0-9 metric tons; B = 10-99 tons; C = 100-999; D = 1000 & Up

Table 4-18. SIC 2819 Industrial Inorganic Chemicals, N.E.C., Distribution of Plant Ages

	28193 Sulfuric Acid			28194 Inorganic Acids			28195 Aluminum Oxide			28196 Aluminum Compounds			28197 Na and K Compounds			28198 Chem. Catalytic Preparation			28199 Other Inorg. Chem. N.E.C.		
Plant Age (years)	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
IV Alabama		2	1		2				1		4	2	1	4	1				2	4	3
X Alaska																					
IX Arizona	1	4											1	1							
VI Arkansas	2	2	2					1	1		2	1		1			1		1	4	1
IX California	1	8	1	2	4	5	1	1		2	5	2	5	11	8	2	9		5	21	15
VIII Colorado											1			1							
I Connecticut											1										
III Delaware			1		1	1						1		2	1					1	1
IV Florida	5	6	4		2	1					2	2	1	3	2		1		1	4	4
IV Georgia	1	2	1	1	3	3					4	2	3	5	4				1	2	4
IX Hawaii		1																		1	
X Idaho		3																	1	2	1
V Illinois	2	5	6	1	3	2				1	2	2	3	6	5	1	1	1	3	13	10
V Indiana	1	3			2						1	1	1	3	2		2			3	4
VII Iowa		1																		2	2
VII Kansas		2				1							1	1	1					2	3
IV Kentucky		1	1	1	2	1		1						1		1	1		1	1	1
VI Louisiana	3	6	2	1	5	4		2	1	1	4	4	2	3	4		1		4	5	6
I Maine	1									1				1						1	
III Maryland		2	2		2	2					1	1	1	3	1		2		1	5	4
I Massachusetts	1			1	1	1		1			1		1	3	2		1		1	1	3
V Michigan		3		1	2	2					3	1		3	3	1	2		1	4	4
V Minnesota		1								1	1									1	1
IV Mississippi		1						1		1	1	1	1	1	1		1		1	4	
VII Missouri		2	1		1						1	1	2	3	2		1		2	6	5
VIII Montana		1															1		1	3	1
VII Nebraska														1						1	
IX Nevada		1			2									2						2	1
I New Hampshire																					
II New Jersey	2	6	3	2	6	5			1	1	4	4	4	10	7	1	5	2	5	11	22
VI New Mexico		2	2		1								2	3	4					5	4
II New York		1	1		3	1		1			2	2	1	5	4		1		4	7	6
IV North Carolina		3	1	1	1						1	1	1	2	4				1	2	1
VIII North Dakota																				1	1
V Ohio	1	5	1	2	4	4				2	3	3	2	5	5	1	3	1	5	9	9
VI Oklahoma		2			1						1			1					1	2	2
X Oregon					1						1			1			1			1	
III Pennsylvania	1	5	2		2	1		1		1	1	2	4	5	6		2		8	7	9
I Rhode Island		1												1						1	
IV South Carolina		1		1	1						1	1		1	1				1	2	
VIII South Dakota																					
IV Tennessee			1		3	1		1		1	2	3	1	3	2		1		2	5	4
VI Texas	3	9	5	4	11	4		2			3	2	1	6	7		2		13	41	21
VIII Utah		1						1			1		1	2	1		1		1	4	2
I Vermont																					2
III Virginia	1	4	2			1					1	2	1	1	3		1			2	3
X Washington	1	1	1	1	1	1				1	2	2	2	2	2		1		2	5	2
III West Virginia		1			5	3								2	2		2			3	2
V Wisconsin											2			2						1	1
VIII Wyoming		2												1						2	3
TOTAL	27	101	41	19	72	44	1	13	4	13	59	43	43	112	[illegible]	7	44	4	70	204	168
Region I	2	1		1	1	1		1		1	2	6	1	5	2		1		1	3	5
II	2	7	4	2	9	6		1	1	1	6	6	5	15	11	1	6	2	9	18	28
III	2	12	7		10	8				1	3	12	6	13	13		7		9	18	19
IV	6	16	9	4	14	6		3	1	2	15	7	8	20	15	1	4		10	24	17
V	4	17	7	4	11	8				4	12	7	6	19	15	3	8	2	10	31	29
VI	8	21	11	5	18	8		5	2	1	10	1	5	14	15		4		19	57	34
VII		5	1		1	1					1	1	3	5	3		1		2	11	10
VIII		4						1			2		1	4	1		2		2	10	7
IX	2	14	1	2	6	5	1	2		2	5	2	6	14	8	2	9		5	24	16
X	1	4	1	1	2	1				1	3	2	2	3	2		2		3	8	3

KEY: A = less than 5 years; B = 5 to 30 years; C = Over 30 years

Table 4-19. SIC 2819 Industrial Inorganic Chemicals, N.E.C., Distribution of Processes

Process Type, No. of Facilities		28193 Sulfuric Acid		28194 Other Acids				28195 Aluminum Oxide		28196 Alum. Cmpds.	28197 Na and K Compounds N.E.C.			28198 Chem. Catalyst	28199 Industrial Inorganic Chemicals											
		Sulfur Burning	Regen	Chromic	HCN	HF	Other	Bauxite Refining	Other	Aluminum Compound Synthesis	K Compound Synthesis	Na Compound Synthesis	Phosphates Synthesis	Catalyst Synthesis	Boron Halides Synthesis	Halogen Synthesis	Co Compound Synthesis	Activated Carbon	Chromates NEC Synthesis	Cu Compound Synthesis	H_2O_2 Synthesis	Fe Compound Synthesis	Mg Compound Synthesis	Mn Compound Synthesis	Phosphorus Compounds	Sulfur and Compounds	Other Compound Synthesis
IV	Alabama	2					2	1		6		6					2								2	3	1
X	Alaska																										
IX	Arizona	1										2															
VI	Arkansas	6						2		3		1		1		3										1	
IX	California	2	7			1	10		2	9	4	20	5	11		1	4	1		3		5	5			18	4
VIII	Colorado									1	1																
I	Connecticut									1																	
III	Delaware		1			1	1			1		4												1		1	
IV	Florida	15					3			4		6		1			2	2							3	2	
IV	Georgia	4					2			6		11	1				1			2		1		1		1	1
IX	Hawaii		1																			1					
X	Idaho	2																		1					2		1
V	Illinois	11	2			1	6			5		12	3	3		1	3			1		6	1	2	1	5	4
V	Indiana	2	2				7			2		5	1	3						2		1				4	1
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	34	32	4	10	14	114	8	10	115	42	192	39	55	3	14	58	10	6	40	7	33	23	19	21	179	45
	Region I	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 4-20. SIC 2819 Industrial Inorganic Chemicals, N.E.C., Distribution of Production

Annual Production 10^3 metric tons		28193 Sulfuric Acid	28194 Inorganic Acids	28195 Aluminum Oxide	28196 Aluminum Compounds	28197 Na and K Compounds	28198 Chem. Catalytic Preparation	28199 Other Inorg. Chem. N.E.C.	2819 as a Whole
IV	Alabama	400	10	700	80	200		50	1,400
X	Alaska								
IX	Arizona	1,000							1,000
VI	Arkansas	430		920	500	10	10	150	2,000
IX	California	1,400	450	40	75	1,500	10	200	3,700
VIII	Colorado				30	150			180
I	Connecticut							20	20
III	Delaware	260	120		65	100		50	600
IV	Florida	9,300			50			80	9,400
IV	Georgia	540	20		60	180		150	950
IX	Hawaii	30						30	60
X	Idaho	1,100						250	1,300
V	Illinois	760	950		150	800	15	230	2,900
V	Indiana	400	80		30	200		40	750
VII	Iowa	400						100	500
VII	Kansas	200	10			90		50	350
IV	Kentucky	230	120	20			40	180	590
VI	Louisiana	4,300	250	2,200	400	420	15	400	8,000
I	Maine	60			30			30	120
III	Maryland	410	80		140	30	15	220	900
I	Massachusetts	60	20	80	30	100		100	390
V	Michigan	100	120		40	450	10	900	1,600
V	Minnesota	90			40			20	150
IV	Mississippi	450		100	80	150		100	880
VII	Missouri	530			40	250		800	1,600
VIII	Montana	260						30	290
VII	Nebraska							10	10
IX	Nevada	130	20			50		30	230
I	New Hampshire								
II	New Jersey	1,600	310		150	800	35	400	3,300
VI	New Mexico	260				3,000		30	3,300
II	New York	140	110	20	30	470		300	1,100
IV	North Carolina	980	10		30	50		100	1,200
VIII	North Dakota							20	20
V	Ohio	540	240		120	300	25	300	1,500
VI	Oklahoma	170			10			60	240
X	Oregon		10		30	50		50	140
III	Pennsylvania	820	50	20	60	300	10	250	1,500
I	Rhode Island	20				20			40
IV	South Carolina	40			20	40		15	110
VIII	South Dakota								
IV	Tennessee	870	80	20	80	270	10	400	1,700
VI	Texas	3,500	520	2,100	600	300		400	7,400
VIII	Utah	120		20	30	600		100	870
I	Vermont							10	10
III	Virginia	640	10		40	120	5	100	910
X	Washington	130	20		50	30		150	380
III	West Virginia	110	60			80		70	320
V	Wisconsin				50	10		30	90
VIII	Wyoming	80				70		10	160
TOTAL		33,000	3,700	6,200	3,200	11,000	200	7,000	64,000
Region I		140	20	80	60	120	0	160	580
II		1,700	420	20	180	1,300	35	700	4,400
III		2,200	320	20	320	630	30	690	4,200
IV		13,000	240	840	400	890	50	1,100	16,000
V		1,900	1,400	0	430	1,800	50	1,500	7,000
VI		8,700	770	5,200	1,500	3,700	25	1,000	21,000
VII		1,100	10	0	40	340	0	960	2,500
VIII		460	0	20	60	820	0	160	1,500
IX		2,600	470	40	75	1,500	10	260	5,000
X		1,200	30	0	80	80	0	450	1,800

Table 4-18 lists the distribution of plant ages in SIC 2819. In each of the seven production subcategories, the majority of plants fall into the 5-30 year age bracket.

Table 4-19 shows the distribution by process types in SIC 2819. The number of processes employed by this industry is large and diversified.

Table 4-20 lists the distribution of production in this industry. The industry as a whole produces about 64,000,000 metric tons per year of products with SIC 28193, sulfuric acid, accounting for over half the total. The two most heavily concentrated areas are EPA Regions IV and VI with 16,000,000 and 21,000,000 metric tons per year, respectively.

According to the 1972 Census of Manufacturers, the establishments primarily engaged in SIC 2819 manufacture average 169 total employees per establishment and 106 production employees per establishment. Seventy percent of the reported establishments have 20 or more employees.

5.0 WASTE CHARACTERIZATION

5.1 Introduction

In this section, the processes, the wastes resulting from each process, and the amounts of hazardous waste generated are described for each segment of the industry. Projections are made for the amounts of hazardous wastes to be produced in 1977 and 1983, and these are based upon two major considerations:

- Changing production patterns within the industry, due to a variety of causes such as developments in markets, in process technology and in raw material supply, and
- the effects of upcoming air and water regulations on the generation of hazardous wastes destined for land disposal

The flow diagrams accompanying the process and waste stream descriptions are presented within the following format:

> Raw materials are on the left and products are on the right. Gaseous emissions are projected upward and waste products, both solid and liquid, are projected downward.

All diagrams are based on 1000 units of mass of the principal product; miscellaneous water uses are not generally quantified. For clarity, several unit operations have, in some cases, been combined in one block. Heavy lines represent the main flow from raw materials to product. The diagrams reflect our technical judgment of typical or usual operations in the given industrial subcategory, rather than those associated in the specific, identifiable plant. Production rate and other data for the assumed typical plant are given in the text accompanying each diagram.

Both process and cooling water use vary with plant location, plant management, process, plant age, and product purity. The exemplary plant water use may often be easily quantified, but the water use in a "typical" plant is usually loosely coupled to the technology of the process, and can therefore differ several fold from specific operating levels.

The water content of the hazardous waste streams destined for land disposal can vary widely for a variety of reasons: e.g., individual operating practice, equipment limitations, local availability of water, and rainfall. Thus only reasonable generalizations can be made about this component. For purposes of estimation, the following water contents were found to be generally prevalent in waste streams from these industries:

(a) filter cake, 20-50% moisture
(b) sludges from settling ponds, 60-80% moisture
(c) slurries, ≥90% moisture
(d) retort or furnace residues, less than 10% moisture

5.1.1 The Hazardous Nature of Waste Streams

The hazardous waste streams selected from these industries were selected to be as consistent as possible with the following published definition of EPA(69): "Hazardous wastes" means any waste or combination of wastes which pose a substantial present or potential hazard to human health or living organisms because such wastes are nondegradable or persistent in nature or because they can be biologically magnified, or because they can be lethal, or because they may otherwise cause or tend to cause detrimental cumulative effects" (underlining added).

For a detailed discussion of the criteria used to determine a "hazardous" waste stream, see the earlier Section 1.1.3 concerning methodology. Generally when a waste stream contains one or more hazardous constituents, in concentrations judged to be significant, the entire waste stream is considered hazardous.

The major area of concern is the group containing the most severely hazardous materials generated by the inorganic chemicals industry. Detailed studies of average, exemplary, and environmentally adequate disposal practices have been conducted. However, most solid waste materials generated by the industry are not severely hazardous, and so are not emphasized in this study. This should not be taken to imply that waste streams other than those deemed to be "hazardous" by virtue of their content of "severely hazardous" or "moderately hazardous" constituents need no landfill precautions. Indeed, some of these waste streams could have detrimental effects on the environment if improperly handled, as for example large amounts of soluble salts such as sodium chloride or calcium chloride as moist solids or concentrated brines. Normally these materials in moderate amounts are not considered to be hazardous and are not so considered in this report. Where materials because of their high concentrations, large amounts, or other special situations at specific locations constitute potential hazards , they have been designated as "hazardous" herein, this has been the case for several calcium fluoride-containing waste streams.

Waste streams other than "severely hazardous" can be grouped into two general categories: the totally non-hazardous, and the moderately hazardous. The general properties of materials falling into these categories and their corresponding disposal recommendations are:

Non-hazardous - Inert solid wastes; i.e. those having no detrimental environmental effects. These wastes should not pose a threat to water quality or human contact in any way (except, possibly esthetic) and hence may be safely disposed of in landfill sites exposed to ground and surface water. Examples of these materials from this report are brick and carbon rubble from process equipment and gypsum solid waste uncontaminated by toxic materials.

Moderately hazardous - Water may become polluted if such wastes are placed in water or if water is allowed to pass through them (discharging a leachate of high mineral content). Landfill sites accepting these wastes must provide for separation of the wastes from underlying or adjacent usable water by natural or artificial barriers. Subsurface flow in the form of springs or seepage should be prevented from entering the disposal area. Disposal areas should be protected by natural or artificial features to assure protection from any washout or inundation which could occur as a result of tides or floods. Surface drainage from tributary areas should be prevented from contacting wastes in the site. To prevent gases and leachate emanating from the landfilled material from adversely affecting local groundwater, natural or artificial barriers should be installed and maximum separation should be provided from the highest anticipated groundwater level.

Implementation of these general recommendations would, in most cases, be sufficient to prevent leachate of high mineral content escaping from landfills containing such wastes.

In some cases in this report wastes streams composed largely of "moderately hazardous" materials have been identified as hazardous waste streams because of the potential hazard involved in the amounts and the locations of the specific instances. Examples of these from this industry are calcium fluoride solid wastes, or calcium fluoride mixed with gypsum.

The following sections discuss each of the segments of the inorganic chemical industry, the processes and wastes involved in each, and the types of wastes.

5.2 Alkalies and Chlorine (SIC 2812)

This segment of the inorganic chemicals industry includes those facilities producing chlorine, sodium and potassium hydroxides, synthetic soda ash, sodium bicarbonate, and potassium and ammonia carbonates. Descriptions of the processes and wastes involved in these subcategories are given below.

5.2.1 Chlorine (SIC 28121)

Within the SIC 281 category, chlorine is produced by five basic processes:

(a) The Mercury Cell and Diaphragm Cell chlor-alkali processes, in which either sodium hydroxide or potassium hydorxide is produced as a co-product.
(b) The Down's cell process, which involves the electrolysis of molten salt and generates metallic sodium as a co-product.
(c) The Kel-Chlor process, which is similar to the diaphragm cell operation except that hydrochloric acid instead of a sodium chloride solution is electrolyzed. Hydrogen is generated as a co-product. This process is currently operational at only one facility and, since its hazardous wastes are similar in nature to those generated by the diaphragm cell, it will not be discussed separately.
(d) The Vicksburg Chemical process in which potassium chloride and nitric acid are reacted to form chlorine nitrosyl chloride, and potassium nitrate as co-products. This process is currently operational in only one facility and, as there are no wastes destined for land disposal, requires no further treatment herein.

In addition to the above, some quantities of by-product chlorine are produced by a process not included in SIC 281, namely the electrolytic manufacture of magnesium (SIC 3339).

5.2.1.1 Diaphragm Cell Process

Sodium chloride brines are first purified by addition of sodium carbonate, flocculating agents, and sodium hydroxide in amounts required to precipitate all the magnesium and calcium contents of the brine. The brine is then filtered to remove the precipitated materials and electrolyzed in a diaphragm cell. Chlorine, formed at one electrode, is collected, cooled, purified, compressed, and sold. The sodium hydroxide formed is subjected to partial evaporation, (which precipitates most of the unreacted sodium chloride from the solution) and then filtered. The collected sodium chloride is recycled to the process, and the sodium hydroxide solutions are further evaporated to yield solid products. The flow diagram for the typical operation of this type is shown in Figure 5-1. An analogous process uses potassium chloride brine to produce a potassium hydroxide (caustic potash) co-product. Some values of materials in this flow diagram have been given ranges, for example sulfuric acid 12(6-35). The parenthetical values are range extremes experienced in the industry. The percentage values given with the sulfuric acid streams refer to their concentrations.

There are several waste streams generated:

(a) Brine purification muds
The muds generated are primarily calcium carbonate, magnesium hydroxide, barium sulfate, and water. Because the solubilities and toxicities of these waste constituents are low, they are not hazardous, and stringent landfill requirements are not appropriate.

(b) Lead salts resulting from wastewater treatment
The lead arises in the effluent due to cell breakdown and corrosion. The wastes generated by wastewater treatment are lead carbonate (solubility 1.1-1.7 mg/l) and basic lead carbonate (solubility 1.7 mg/l). The composition of the solid waste generated by wastewater treatment is quite variable from plant-to-plant and hence the treatment and effluents of treatment are not given in Figure 5-1. However, typically a wastewater treatment removes over 90% of the lead content prior to discharges. (Appendix A details the properties of these compounds). Lead carbonate and basic lead carbonate comprise the major constituents of the waste stream, and the overall properties of the waste are the same as those described for the individual components. Because of the toxicity and solubilities of these waste constituents, and because of the bioaccumulative phenomena for lead, the waste material must be completely isolated from the environment upon land disposal.

(c) Asbestos wastes from cell diaphragms Asbestos is hazardous to man when inhaled and, possibly, when taken orally. However it is completely insoluble in a landfill and the only land disposal requirement is that the surface be protected from the erosional forces of wind and rain. The

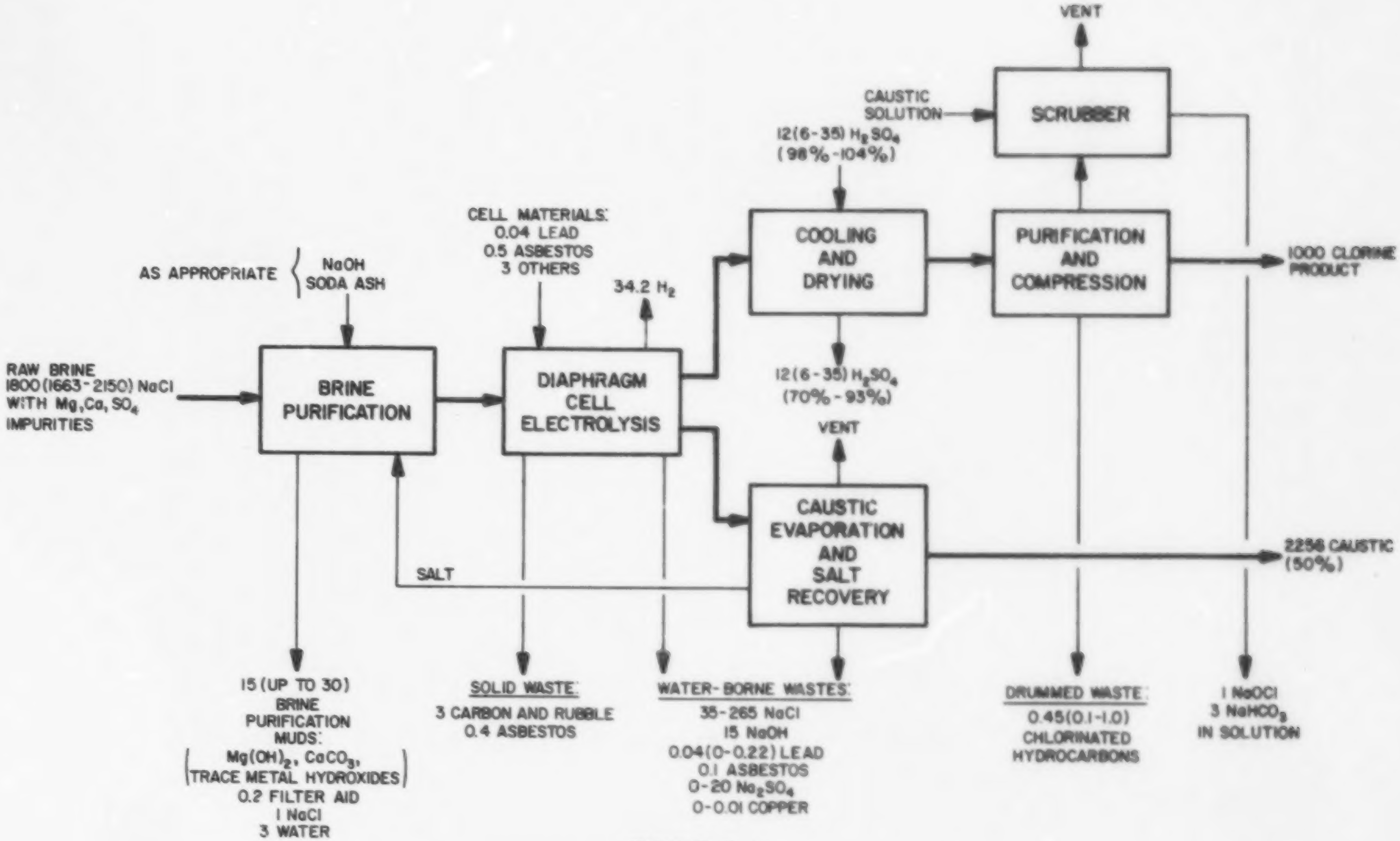

FIGURE 5-1
CHLOR-ALKALI MANUFACTURE
DIAPHRAGM CELL PROCESS

chemical, physical, and biological properties of asbestos are detailed in Appendix A.

(d) Chlorinated hydrocarbon wastes These arise from reaction of chlorine with the carbon anode. Chlorinated hydrocarbon wastes exhibit the properties described in Appendix A.

The principal growth in the chlorine industry can be expected to take place in this segment (65-67). Water and air regulations have little or no impact on hazardous wastes generated, and process technology is under rapid development in several areas having to do with construction materials for the cells. Lead and chlorinated hydrocarbon wastes are being reduced by the use of coated metal anodes (otherwise known as dimensionally stable anodes), and these are gradually replacing graphite anodes in existing plants. Indeed, all new construction is being carried out with coated metal anodes, and asbestos wastes will be reduced when plastic microporous separators become commercially acceptable. We estimate this separator changeover to be well under way by 1977, but complete changeover not to be attained for at least a decade, based on discussions with industry.

The typical diaphragm plant is large (upward of 500 tons per day), and the trend in recent times has been to very large plants with capacities greater than 1000 tons per day. They tend to be distributed according to local economic factors for much the same reason as the mercury cell plants discussed below. The typical plant, while also 5 to 30 years old, is relatively newer than a mercury-cell plant.

5.2.1.2 Mercury Cell Chlor-Alkali Process

The typical mercury cell plant has a production rate of 275 tons per day and is 5 to 30 years old. A typical location is near cheap power, a salt source, and a market for the chlorine; but localization is not otherwise apparent.

In the mercury cell process, caustic and chlorine are produced from salt or potassium chloride raw materials depending on whether caustic soda or caustic potash is to be produced. The raw material is dissolved and purified by the addition of barium carbonate, soda ash, and lime to remove magnesium and calcium salts and sulfates prior to electrolysis. The insolubles formed by addition of the treatment chemicals are filtered from the brine, and the brine is then fed to the mercury cell, in which chlorine is liberated at one electrode and a sodium-mercury amalgam is formed at the other.

The chlorine formed is cooled, dried in a sulfuric acid stream, purified to remove chlorinated organics, compressed and sold. The mercury-sodium amalgam (also formed during electrolysis) is sent to a "denuder" where it is treated with water to decompose the amalgam. Sodium hydroxide and hydrogen are formed in the reaction. The mercury liberated is returned to the electrolysis cells. The hydrogen in a typical plant is flared through, in others, it is cooled, scrubbed to remove traces of mercury, compressed, and sold.

The sodium or potassium hydroxide formed at the denuders is filtered, concentrated, and sold, and waste brines emerging from the electrolysis cells are re-saturated and recycled. In some instances, the weak brine is treated to precipitate mercury before recycle, but not typically.

The flow diagram for the usual operation of this process is given in Figure 5-2. There are several waste streams involved, some of which are hazardous:

(a) Brine purification muds - These are often contaminated with mercury in a typical amount of 0.005 kg per metric ton of chlorine and a range of 0-0.015 kg/kkg. Whether or not these muds are hazardous varies from plant-to-plant in this industry depending on process details. They range from no mercury content to an average top value of 100 ppm. This latter is judged to be hazardous.

(b) Sludges from treatment of brine to remove mercury compounds. They contain free mercury or mercury sulfide. The mercury content is typically 0.058 kg/metric ton of chlorine.

(c) Chlorinated hydrocarbons from chlorine purification in the amounts shown in Figure 5-2.

Other losses of mercury in these plants include losses to the atmosphere as an impurity, in products, and in the waste water discharge.

Of the waste streams which are potential candidates for land disposal, two definitely fall in the severely hazardous category. They are the chlorinated hydrocarbon waste (c) and the sludges from mercury removal treatment (b). For both waste streams the concentration of hazardous constituents is high enough that the overall biological properties of the wastes are very similar to the individual constituents. Specific data on both the properties of mercury and its compounds and on the chlorinated hydrocarbons is given in Appendix A.

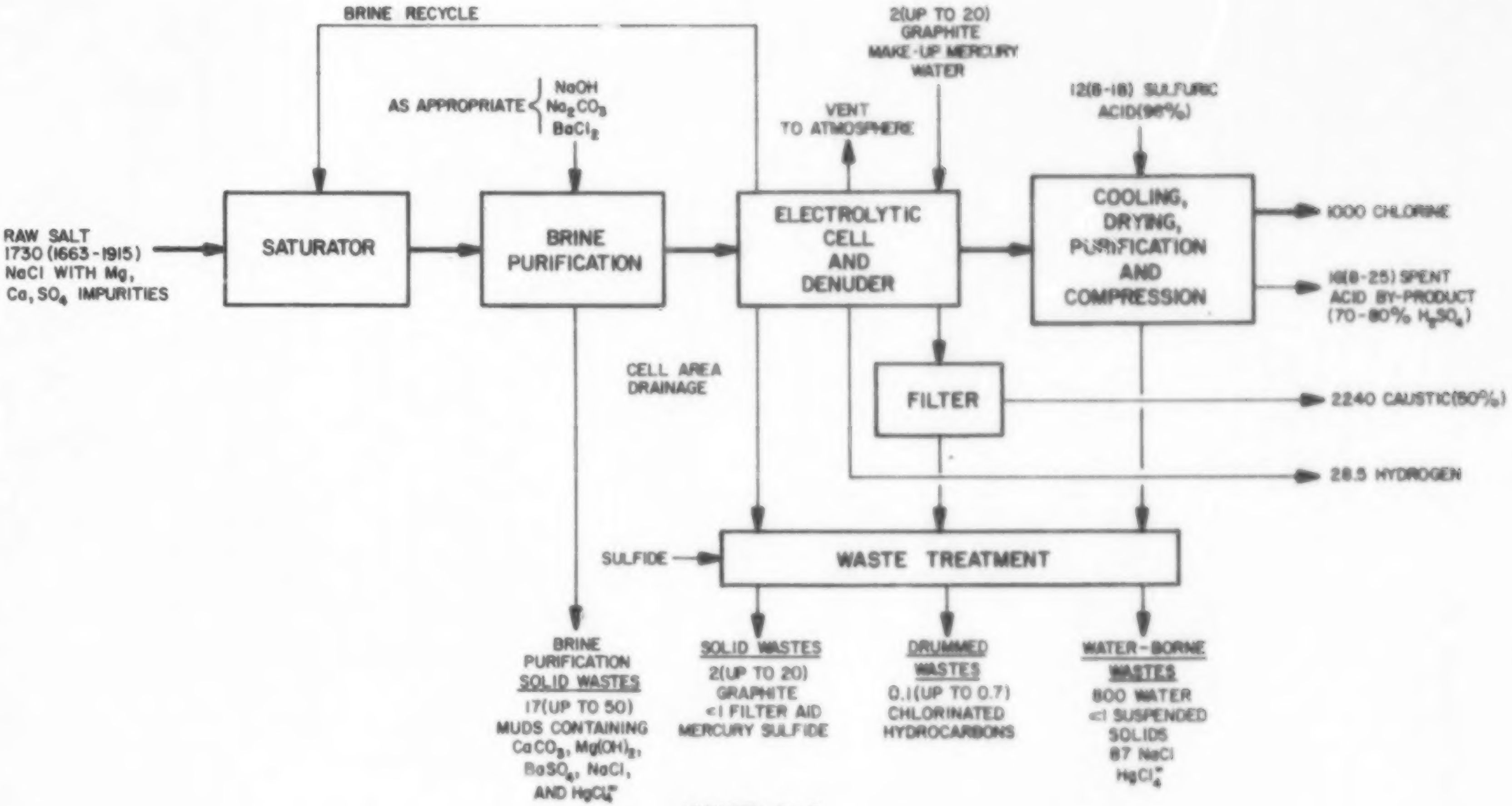

FIGURE 5-2

CHLOR-ALKALI MANUFACTURE
MERCURY CELL PROCESS

The mercury contamination of brine purification muds varies throughout the industry. Some plants separate electrolysis cell wastes from primary brine purification wastes, and thus the large quantities of such wastes (composed primarily of calcium carbonate, magnesium hydroxide and barium sulfate, which are non-hazardous) do not contain mercury and may be landfilled with less strenuous requirements. These plants then apply mercury removal technologies to the smaller, more concentrated waste stream from electrolysis and denuding operations and these can therefore be disposed of in a secure landfill.

Facilities segragating the two waste streams generate significant tonnages per year of brine sludge containing as much as 100 ppm mercury (68). Although diluted in the waste, the problem of controlling the escape of mercury to the environment remains. The mercury concentration in surface runoff and leachate from this landfilled waste would exceed acceptable limits, and, consequently, safeguards to prevent contamination of surface and groundwaters are required. These wastes are considered to be hazardous.

Because of the danger associated with mercury pollution, mercury cell production is being shifted to diaphragm cell production (65-67). Through the period to 1977, conversion or shut-downs in mercury cell operations are occurring in Texas, Louisiana, New York, Washington, and Tennessee (64, 67). New capacity is being added (in this period) in Alabama and Maine (64, 67). Between 1971 and 1983, it can be assumed that mercury cells production in several states will be completely abandoned.

Waste generation at operating facilities can be expected to experience the following trends:

(a) Mercury in water discharge - by 1977, this will be reduced to 0.00014 kg per metric ton of chlorine production and by 1983, the discharge of mercury to water overall will be an order of magnitude lower, reaching effectively zero in some plants.

(b) Brine sludges - the relative mercury content will be reduced to 50 percent of the current level by 1977 and to 20 percent of the current level by 1983.

(c) Process sludges - mercury-rich precipitates not reclaimed will be reduced to about one-half of the current level by 1977. By 1983, 99 percent recovery of mercury in these sludges will be achieved in some plants, and approximately 90 percent in the others.

(d) The chlorinated hydorcarbons generated will be reduced to 50 percent and 20 percent of the present levels, by 1977 and 1983, respectively.

5.2.1.3 Down's Cell Process

Down's Cell chlorine is produced in 5 plants in five states. The typical plant has a daily capacity of about 200 tons of chlorine. All five plants are 5 to 30 years old.

In the Down's cell process, sodium and chlorine are manufactured by electrolysis of molten sodium chloride. After salt purification to remove calcium and magnesium salts and sulfates, the sodium chloride is dried and fed to the cell, where calcium chloride and other minor bath components are added to give a low-melting $CaCl_2 \cdot NaCl$ eutectic, which is then electrolized. Sodium is formed at one electrode, collected as a liquid, filtered, and sold. The chlorine liberated at the other electrode is first water washed (for $SiCl_4$ hydrolysis) and then dried with sulfuric acid purified, compressed, liquified, and sold.

The molten sodium-calcium metal mixture is then cooled and a calcium sludge is separated by filtration. At two plants this material is wasted and goes to sea disposal in drums. At the other three plants proprietary processes treat these materials, return part or all to the process, and any residue left over has been stated by the manufacturers to be non-hazardous. Details of this have not been divulged.

The flow diagram for the usual operation of this process is given in Figure 5-3.

There are several wastes generated by this process:

(a) Brine purification sludges - these consist of calcium carbonate, magnesium hydroxide and in some cases barium sulfate. The brine purification muds operated by Down's cell facilities are similar to those described earlier and are non-hazardous.

(b) Sodium-calcium sludges - These arise from the filtration of product sodium. These wastes are considered hazardous because of their reactivity with water. These sludges must be disposed of under carefully-controlled conditions to avoid explosions or fires. We envision no technology changes which will alter the amounts of sodium-calcium sludges generated through 1983. The impact of air and water regulations on the wastes generated appear to be negligible.

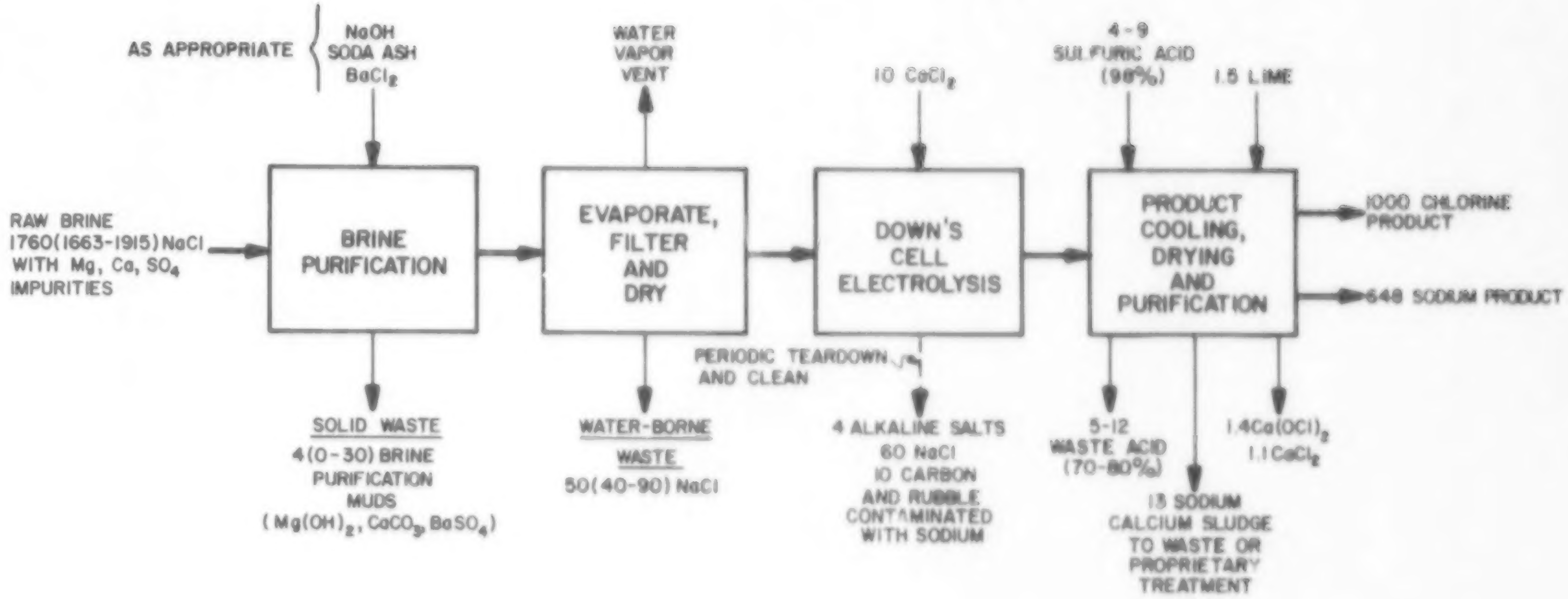
AS APPROPRIATE
NaOH
SODA ASH
$BaCl_2$
WATER VAPOR VENT
10 $CaCl_2$
4-9 SULFURIC ACID (98%)
1.5 LIME
RAW BRINE 1760(1663-1915) NaCl WITH Mg, Ca, SO_4 IMPURITIES
BRINE PURIFICATION
EVAPORATE, FILTER AND DRY
DOWN'S CELL ELECTROLYSIS
PRODUCT COOLING, DRYING AND PURIFICATION
1000 CHLORINE PRODUCT
648 SODIUM PRODUCT
PERIODIC TEARDOWN AND CLEAN
SOLID WASTE
4(0-30) BRINE PURIFICATION MUDS
($Mg(OH)_2$, $CaCO_3$, $BaSO_4$)
WATER-BORNE WASTE
50(40-90) NaCl
4 ALKALINE SALTS
60 NaCl
10 CARBON AND RUBBLE CONTAMINATED WITH SODIUM
5-12 WASTE ACID (70-80%)
13 SODIUM CALCIUM SLUDGE TO WASTE OR PROPRIETARY TREATMENT
1.4 $Ca(OCl)_2$
1.1 $CaCl_2$

FIGURE 5-3

SODIUM AND CHLORINE MANUFACTURE
DOWN'S CELL PROCESS

(c) Wastes from cell maintenance and replacement are contaminated with small amounts of sodium metal. This waste is allowed to remain in the open in an isolated area exposed to the weather to allow moisture to penetrate and react with the sodium.
(d) Sodium chloride fines from steps prior to fusing are landfilled on-site, where dry salt is used as raw material.
(e) Excess calcium hypochlorite is decomposed in ponds.
(f) Effluent from washing area goes to wastewater treatment system.

All producers are faced with providing a dedicated storage because of the potential for sodium inclusion. Storage is on-site initially until weathering is complete, then the waste could be removed to a commercial disposal site as a non-hazardous waste.

5.2.2 Synthetic Sodium Carbonates (SIC 28122)

5.2.2.1 Synthetic Soda Ash (Solvay Process)

The typical synthetic soda ash plant has a capacity of about 1500 tons per day and is over 30 years old.

Soda ash is produced either by the mining and refining of impure sodium sesquicarbonate (from ore - SIC 1474), or by the Solvay process-where soda ash is produced from limestone and salt with the aid of ammonia. This process is shown in the accompanying flow diagram (Figure 5-4). The Solvay process involves a reaction in aqueous solution (under pressure) between ammonia, brine (NaCl), and carbon dioxide to yield sodium bicarbonate, which is then converted to soda ash by heating. Ammonia is recovered by the addition of slaked lime to the used liquor. The saturated brine is purified of other metal ions by precipitation, and then picks up ammonia in an absorber tower. Ammoniated brine is reacted with carbon dioxide in a carbonating tower, and the resulting bicarbonate precipitates as the sodium salt, forming a slurry. The slurry is filtered to remove the solid bicarbonate which is calcined to yield the light ash product. Dense ash is made by successive hydration and dehydration of the light ash. The carbon dioxide and ammonia are recycled. The wastes consist of salt brine purification muds which contain calcium carbonate and magnesium hydroxide and the ammonia distiller bottoms which consist predominantly of calcium carbonate with lesser amounts of magnesium carbonate, silica, and alumina. The waste brines are always discharged as a water effluent except when evaporated to dryness for sale. The solids are

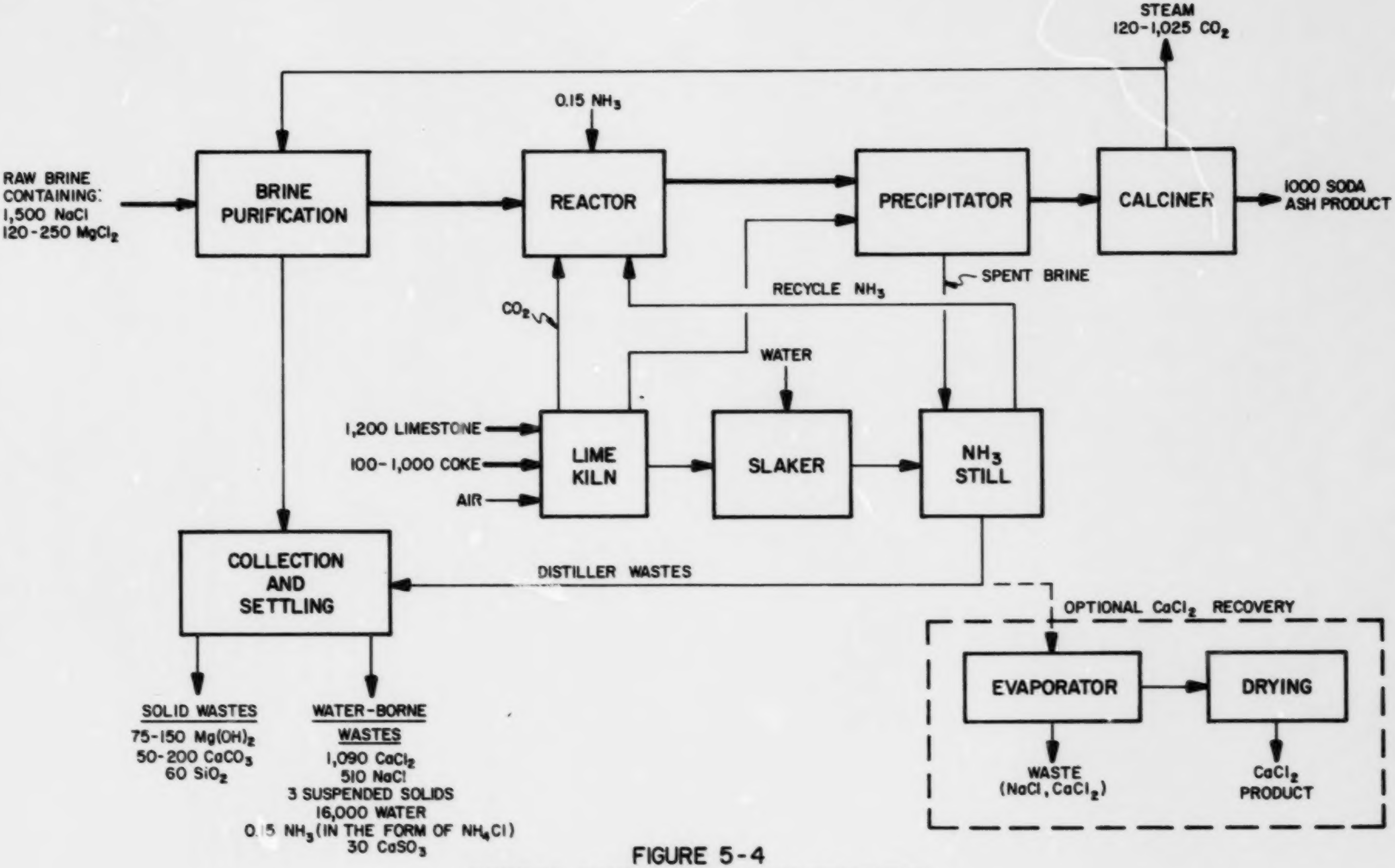

FIGURE 5-4
SODIUM CARBONATE MANUFACTURE
BY THE SOLVAY PROCESS

land disposed in extensive settling bed systems. These land destined wastes are not hazardous.

5.2.2.2 Sodium Bicarbonate Process

All such production is located either at Solvay process soda ash plants or at Trona refineries. The typical plant is 150 tons per day, and is the same age as the parent plant--that is, namely over 30 years for Solvay locations and less than 10 years for Trona locations.

This item is produced by reaction of soda ash with carbon dioxide in water under pressure. The bicarbonate precipitates from the solution and is filtered, washed, dried, and packaged. The only process wastes are water-borne and consist of aqueous solutions containing bicarbonate and soda ash. These are neutralized prior to discharge. There are no hazardous wastes generated. The flow diagram is shown in Figure 5-5.

5.2.3 Sodium Hydroxide (SIC 28123)

This product is produced solely as a co-product of chlorine manufacture. The associated wastes are wholly attributed to SIC Code 28121.

5.2.4 Other Alkalies (SIC 28124)

5.2.4.1 Ammonium and Potassium Carbonates

Potassium carbonate is made in conjunction with the production of chlorine at plants electrolyzing potassium chloride (see SIC 28121). The caustic liquor is carbonated by carbon dioxide under pressure. No wastes other than those attributable to the Diaphragm Cell Process are generated.

Ammonium bicarbonate is recovered from process streams of the Solvay Process for manufacture of soda ash (see SIC 28122). No additional wastes are generated.

5.2.4.2 Potassium Hydroxide

This product is produced solely as a co-product of chlorine manufacture. The wastes associated are wholly attributed to SIC Code 28121.

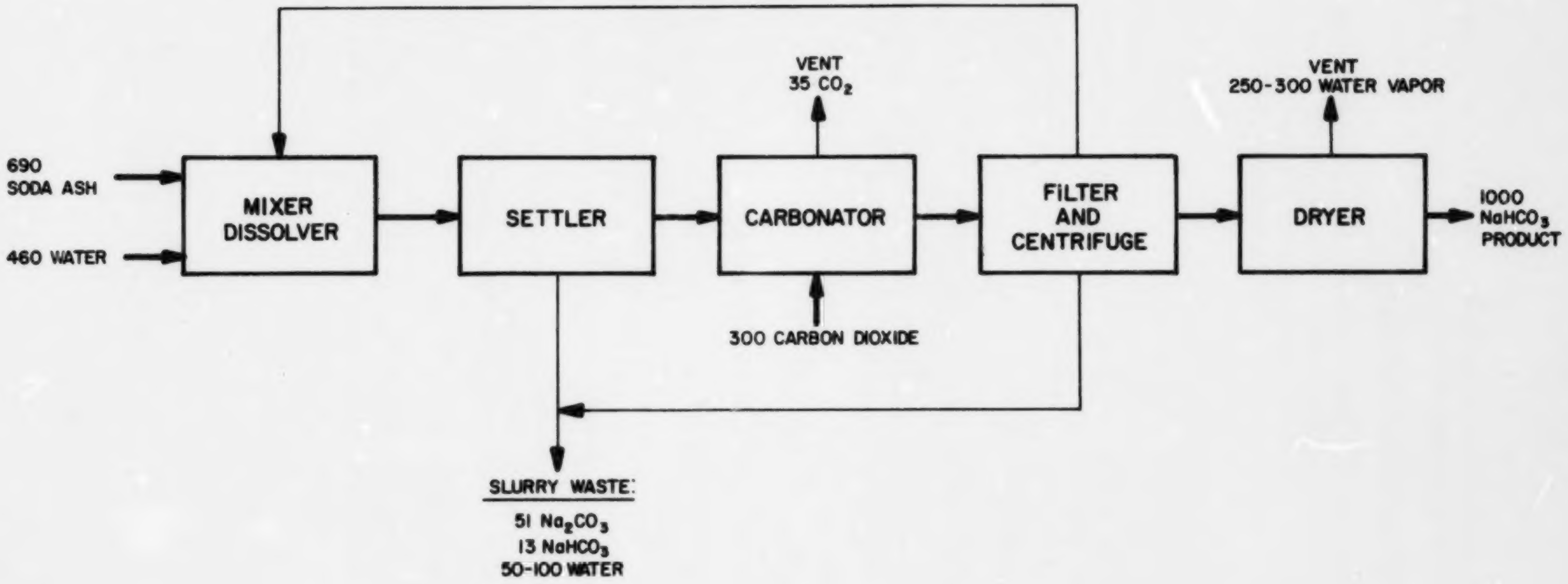

FIGURE 5-5

SODIUM BICARBONATE MANUFACTURE

5.2.5 Aggregate SIC 2812 Hazardous Wastes to Land Disposal

The amounts of the constituents of the several waste streams containing hazardous materials in sufficient quantities to be hazardous in total are shown for the typical or usual operation in the flow diagrams in the preceding sections. The values given are relative to the product rate; that is they are numerically equivalent to either kilograms per metric ton of product or pounds per 1000 pounds of product. The hazardous waste streams from this industrial category are all from SIC 28121 and are:

- mercury-contaminated brine purification muds from the Mercury Cell process,
- mercury-rich wastes from treatments and cleanings elsewhere in the Mercury Cell process,
- chlorinated hydrocarbons from both the Mercury Cell and Diaphragm Cell process,
- asbestos separator wastes from the Diaphragm Cell process,
- lead-containing treatment wastes from the Diaphragm Cell process, and
- explosively reactive or flammable metallic sodium and calcium sludges from the Down's Cell process.

The amounts of moisture in these waste streams are given generally as:

no water: chlorinated hydrocarbons, sodium-calcium sludges.
30-60% water: mercury, lead, and asbestos containing muds, filter cakes, and sludges.

The Table 5-1 lists the aggregated hazardous waste streams of SIC 2812 on a state-by-state, regional, and total U.S. basis and the amounts of the various hazardous constituent materials is estimated as currently valid. Local situations in each state which deviate from the "typical" are taken into account insofar as possible. The data of this table is a mix of the most reliable and the more consistent entries from several sources:

- calculated from consistent manufacturers data
- estimated from fragmentary or equivocal manufacturer's data
- vol. XIV of EPA-670/2-73-053 (August 1973)
- estimated from waste disposal contractor's data
- our own estimates

Table 5-1. Hazardous Wastes Currently Destined for Land Disposal From Alkalies and Chlorine, (metric tons per year, dry basis)

	Diaphragm Cell Solids			Mercury Cell Solids		Chlorinated Hydrocarbons	Sodium/ Calcium Sludge	Total Hazardous Wastes
	Total	Asbestos Content	Lead Content	Total	Mercury Content			
IV Alabama				4,600	30	110		4,700
X Alaska								0
IX Arizona								0
VI Arkansas								0
IX California	20	6	3			4		24
VIII Colorado								0
I Connecticut								0
III Delaware				4,400	13	50		4,400
IV Florida								0
IV Georgia	30	14	8	4,200	14	60		4,300
IX Hawaii								0
X Idaho								0
V Illinois				1,100	6	11		1,100
V Indiana								0
VII Iowa								0
VII Kansas	100	29	16			16		120
IV Kentucky				6,000	32	70		6,000
VI Louisiana	1,000	800	220	7,000	31	510		8,500
I Maine				500	12	20		500
III Maryland								0
I Massachusetts								0
V Michigan	300	190	50			110		400
V Minnesota								0
IV Mississippi								0
VII Missouri								0
VIII Montana								0
VII Nebraska								0
IX Nevada	50	19	11			11		60
I New Hampshire								0
II New Jersey	100	29	16	5,500	16	75		5,700
VI New Mexico								0
II New York	100	55	30	2,100	13	100	810	3,000
IV North Carolina	20	7	4	50	6			70
VIII North Dakota								0
V Ohio	1,300	80	45	660	4	50		2,000
VI Oklahoma								0
X Oregon	40	20						40
III Pennsylvania								0
I Rhode Island								0
IV South Carolina								0
VIII South Dakota								0
IV Tennessee	50	25		5,000	20	80	640	5,800
VI Texas	1,900	830	460	100	20	550		2,600
VIII Utah								0
I Vermont								0
III Virginia	20	7	4					20
X Washington	100	70	15	1,700	13	60		1,900
III West Virginia	300	160	90	2,200	15	150		2,700
V Wisconsin	10	5	3	2,900	22	20		2,900
VIII Wyoming								0
TOTAL	5,400	2,300	980	48,000	270	2,000	1,500	57,000
Region I				500	12	20		500
II	200	84	46	7,600	29	175	810	8,700
III	320	170	94	6,600	28	65		7,100
IV	100	46	12	20,000	100	320	640	21,000
V	1,600	280	100	4,700	32	200		6,400
VI	2,900	1,600	680	7,100	51	1,100		11,000
VII	100	29	16			16		120
VIII								
IX	70	25	14			15		84
X	140	90	15	1,700	13	13		1,900

The hazardous constituents in two cases (lead and mercury) are given in terms of the amount of the chemical element since the hazardous nature of these materials is specific to the chemical elements, whether or not they are actually in elementary or combined form in the waste stream. Chlorinated hydrocarbons are a generic class of chemical compounds hazardous because of their combined chemical form and are given as such. Asbestos is a natural fibrous mineral material of complex chemical structure, and is given as such. The sodium-calcium sludge is a flammable mixture that is given in total.

The data are collected into four groups of waste streams as given in the following table. Essentially, this represents the four hazardous waste stream problems from these industries:

(a) The asbestos and lead-contaminated solid wastes from the brine treatments and cell cleanouts and repairs of the Diaphragm Cell process.
(b) The mercury-contaminated solid wastes from brine purification, process waste treatment, and cell room cleanup of the Mercury Cell process.
(c) The chlorinated hydrocarbon waste separated from both the Diaphragm Cell process and the Mercury Cell process.
(d) The explosive, flammable, sodium-calcium sludge cleanout from the Down's cell process.

The asbestos, lead, and mercury contents of the first two streams are also given, as is the total of the hazardous waste streams from this industry subcategory (SIC 2812).

The largest amounts of hazardous waste streams now disposed of on land from the alkalies and chlorine industries (SIC 28121) are from the Mercury Cell process and amount to nearly 50,000 metric tons (55,000 short tons) per year, dry basis This is nearly 88 percent of the estimated total from the whole SIC subcategory of 57,000 metric tons (63,000 short tons) per year, dry basis. Since a large fraction of these wastes are located at the bottoms of settling ponds, the estimated total weight (moisture included) is of low significance, but for purposes of record are given as 110,000 metric tons (120,000 short tons) per year for SIC 2812 as a whole.

5.2.6 Projection of SIC 2812 Hazardous Wastes to 1977 and 1983

An overall growth in the chlorine-producing industries is expected through 1983 because of the expanding use of chlorine in the treatment of drinking water, the treatment of wastes, and the manufacture of plastics. This subcategory is responsible for the hazardous wastes in SIC 2812. The other segments of 2812 (i.e., synthetic sodium carbonates and miscellaneous other alkalies) are not expected to develop any processes or treatments in this period that will generate hazardous wastes destined for land disposal.

The individual growth factors used in the forward projection of the SIC 2812 wastes were mentioned earlier in the individual process descriptions and include:

- no new starts in the Mercury Cell process.
- all new growth (for chlorine) in the Diaphragm Cell process,.
- the gradual replacement of carbon anodes with coated metal anodes,
- the eventual use of synthetic separators to replace asbestos separators,
- little growth in the Down's Cell process,
- increasingly effective recovery of mercury in the Mercury Cell process.

The major effects of water and air regulations have already been experienced by these industries insofar as generation of large amounts of hazardous wastes for land disposal is concerned. The further amounts of mercury, lead and asbestos that will be removed from discharges due to the application of the 1977 and 1983 restrictions will be small compared to that already removed to land-destined wastes. The reduction in the use of carbon anodes will also cause a reduction in the generation of chlorinated hydrocarbon wastes.

Tables 5-2 and 5-3 give the projected amounts of wastes in the same format as was presented in Table 5-1. State-by-state, regional and total U.S. aggregates are given for the four types of waste streams and for the total hazardous waste to land disposal. The trend of total amounts of hazardous wastes in metric tons per year (short tons per year) projected for SIC 2812 are summarized as follows:

Table 5-2. Hazardous Wastes Expected to be Destined for Land Disposal in 1977 From SIC 2812, Alkalies and Chlorine (metric tons per year, dry basis)

		Diaphragm Cell Solids			Mercury Cell Solids				
		Total	Asbestos Content	Lead Content	Total	Mercury Content	Chlorinated Hydrocarbons	Sodium/ Calcium Sludge	Total Hazardous Wastes
IV	Alabama	60	53		4,600	19	60		4,700
X	Alaska								0
IX	Arizona								0
VI	Arkansas								0
IX	California	20	9	3			3		20
VIII	Colorado								
I	Connecticut								
III	Delaware	30	22		4,400	7	21		4,400
IV	Florida								0
IV	Georgia	60	45	6	4,200	8	33		4,300
IX	Hawaii								0
X	Idaho								0
V	Illinois	10	6		1,100	2	6		1,100
V	Indiana								0
VII	Iowa								0
VII	Kansas	50	40	12			12		60
IV	Kentucky	40	34		6,000	11	35		6,100
VI	Louisiana	1,500	1,200	320	7,000	7	350		8,900
I	Maine				500	4	15		500
III	Maryland								0
I	Massachusetts								0
V	Michigan	300	260	74			75		400
V	Minnesota								0
IV	Mississippi								0
VII	Missouri								0
VIII	Montana								0
VII	Nebraska								0
IX	Nevada	40	27	8			8		50
I	New Hampshire								0
II	New Jersey	90	70	12	5,500	9	40		5,600
VI	New Mexico								0
II	New York	200	120	22	2,100	7	50	830	3,100
IV	North Carolina	30	18	3	50	6	13		100
VIII	North Dakota								0
V	Ohio	180	120	33	660	2	40		900
VI	Oklahoma								0
X	Oregon	40	21						40
III	Pennsylvania								0
I	Rhode Island								0
IV	South Carolina								0
VIII	South Dakota								0
IV	Tennessee	70	53		5,000	10	8	660	5,700
VI	Texas	1,800	1,300	330	100	5	360		2,300
VIII	Utah								0
I	Vermont								0
III	Virginia	15	10	3					15
X	Washington	100	80	11	1,700	5	14		1,800
III	West Virginia	300	260	65	2,200	9	64		2,600
V	Wisconsin	30	15	2	2,900	5	10		2,900
VIII	Wyoming								0
TOTAL		5,000	3,800	900	48,000	120	1,200	1,500	56,000
Region I					500	4	15		500
II		300	200	35	7,600	16	90	830	8,700
III		350	300	70	6,600	16	90		7,000
IV		260	200	9	20,000	54	150	660	21,000
V		520	400	110	4,700	9	130		5,300
VI		3,330	2,500	650	7,100	12	710		11,200
VII		50	50	12			12		60
VIII									
IX		60	40	11			11		70
X		150	100	11	1,700	5	14		1,800

Table 5-3. Hazardous Wastes Expected to be Destined for Land Disposal in 1983 From SIC 2812, Alkalies and Chlorine (metric tons per year, dry basis)

		Diaphragm Cell Solids			Mercury Cell Solids		Chlorinated Hydrocarbons	Sodium/ Calcium Sludge	Total Hazardous Wastes
		Total	Asbestos Content	Lead Content	Total	Mercury Content			
IV	Alabama	40	28	5	4,600	1	5		4,600
X	Alaska								0
IX	Arizona								0
VI	Arkansas								0
IX	California	10	5	1			1		10
VIII	Colorado								0
I	Connecticut								0
III	Delaware	15	12		4,400	0.3	2		4,400
IV	Florida								0
IV	Georgia	30	24	3	4,200	0.4	3		4,200
IX	Hawaii								0
X	Idaho								0
V	Illinois	5	3		1,100	0.1	1		1,100
V	Indiana								0
VII	Iowa								0
VII	Kansas	30	22	6			1		30
IV	Kentucky	20	18	3	6,000	0.4	3		6,000
VI	Louisiana	900	630	170	7,000	0.6	36		7,900
I	Maine				500	0.2	1		500
III	Maryland								0
I	Massachusetts								0
V	Michigan	200	140	40			8		200
V	Minnesota								0
IV	Mississippi								0
VII	Missouri								0
VIII	Montana								0
VII	Nebraska								0
IX	Nevada	20	14	4			1		20
I	New Hampshire								0
II	New Jersey	50	37	6	5,500	0.4	4		5,600
VI	New Mexico								0
II	New York	80	65	12			2	880	1,000
IV	North Carolina	15	10	1	50	0.1	1		70
VIII	North Dakota								0
V	Ohio	100	66	18			4		100
VI	Oklahoma								0
X	Oregon	20	11						20
III	Pennsylvania								0
I	Rhode Island								0
IV	South Carolina								0
VIII	South Dakota								0
IV	Tennessee	40	28		5,000	0.4	3	700	5,700
VI	Texas	1,000	690	180			36		1,000
VIII	Utah								0
I	Vermont								0
III	Virginia	8	5	1			1		10
X	Washington	60	42	6			6		70
III	West Virginia	180	140	35	2,200	0.3	35		2,400
V	Wisconsin	10	8	1			1		10
VIII	Wyoming								0
TOTAL		2,800	2,000	490	41,000	4	160	1,600	45,000
Region I					500	0.2	1		500
II		130	100	18	5,500	0.4	6	880	6,600
III		200	160	36	6,600	0.6	38		6,800
IV		150	110	7	20,000	2.3	15	700	21,000
V		310	220	60	1,100	0.1	14		1,400
VI		1,900	1,300	350	7,000	0.6	72		8,900
VII		30	22	6			1		30
VIII									0
IX		30	22	5			2		30
X		80	53	6			6		90

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Period	Current	1977	1983
dry basis	57,000 (63,000)	56,000 (62,000)	45,000 (50,000)
moisture included	110,000 (121,000)	109,000 (120,000)	89,000 (98,000)

Thus, although the industry as a whole is expected to grow very significantly, the amounts of hazardous wastes destined for land disposal are expected to decrease-principally because of process technology developments within the chlor-alkali segment. The above wastes consist principally of sludges, filter cakes and dewatered muds and the overall moisture content estimate was based on these (approximately 50%).

5.3 Industrial Gases (SIC 2813)

The gases produced in this industry segment are those generally intended for sale in compressed, liquid or solid form. These are: acetylene, air separation products (including the noble gases), carbon dioxide, hydrogen, carbon monoxide, helium, and nitrous oxide. The other gases are in other SIC categories, e.g., fluorine and sulfur dioxide which are in 2819, ammonia in 2842 and 2873, and chlorine in 2812.

5.3.1 Acetylene (SIC 28123)

Until recently, most acetylene was made by the reaction of calcium carbide with water:

$$Ca_2C_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

When carried out as a batch process, the calcium hydroxide wastes consist of a lime slurry containing about 90% water. In the dry generation process, more nearly stoichiometic quantities are used and the heat of the reaction is largely dissipated by water evaporation, leaving the by-product lime in a dry, fairly easily handled state. This lime may be recycled to the carbide process. In neither case are the wastes hazardous. The calcium carbide process is the only one principally carried out in SIC Code 281 establishments and is shown in the accompanying flow diagram, see Figure 5-6. The production from this process is the principal volume and is detailed earlier in the Section 4 tables.

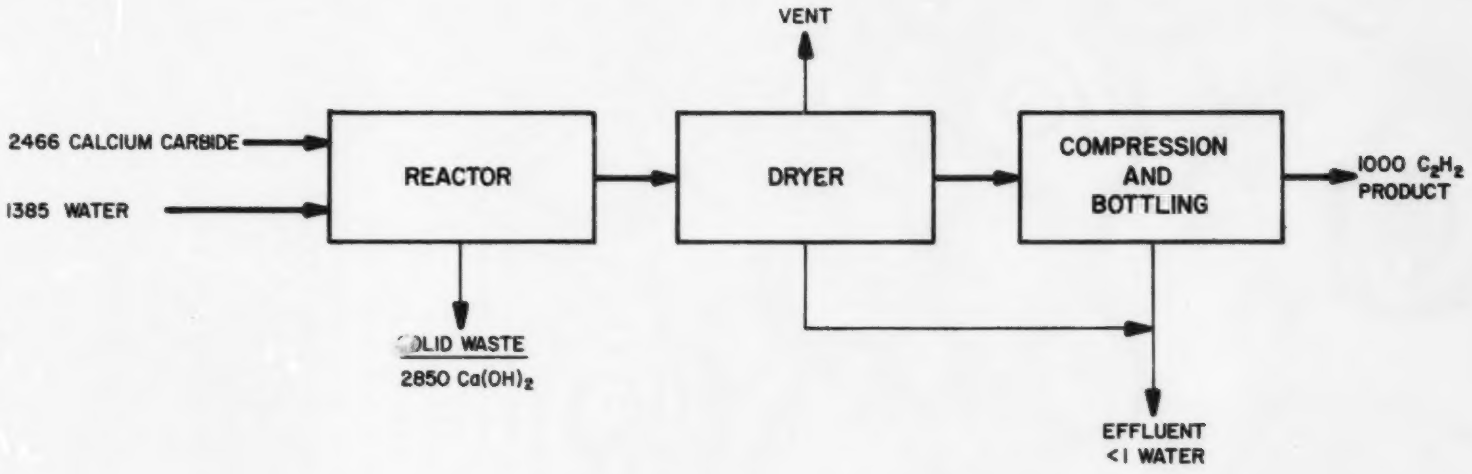

FIGURE 5-6
ACETYLENE MANUFACTURE

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Other methods of acetylene production include (1) from paraffin hydrocarbons by pyrolysis (Wulff Process), (2) from natural gas by partial oxidation (Sachsse Process), and (3) from hydrocarbons by Arc Process.

The Wulff Process is described (for a butane feed) by the following reactions:

$$C_4H_{10} + \text{steam}\ C_2H_2 + C_2H_4 + CO + H_2$$

$$C_2H_4 = C_2H_2 + H_2$$

$$2CH_4 = C_2H_2 + 3H_2$$

Most off-gases, (principally ethylene, carbon monoxide, hydrogen, and methane) are gases used as fuel for the steam boiler, for combustion chamber and heating, or other in-plant use. There is a small amount of organic tar originating in the furnace and the electrostatic precipitator, but these wastes are not severe hazards. This process, the Arc Process, and the Sachsse Process generally are carried out in SIC Code 286 (Industrial Organic Chemicals) establishments.

The Sachsse Process may be described by the following reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$2CH_4 = C_2H_2 + 3H_2$$

This cracking process may be carried out using a variety of hydrocarbon feed stocks; e.g., natural gas, LPG, naphtha, fuel oil or even crude oil. The sooty waste emanates from the burner and the soot filter. A widely used variation of the Sachsse process is the BASF process.

The Arc Process is generally not favored for U.S. production of acetylene because of the high power requirements and associated costs. The Huck Process, which employs one design of an arc furnace, is not operated in the U.S. In fact, the DuPont arc process is the only arc process used in the U.S., and it is currently shut down.

The typical acetylene plant has a 50 ton per day capacity and is 5 to 30 years old.

5.3.2 Carbon Dioxide (SIC 28133)

This product is recovered from limestone calcination and as a by-product of hydrogen generation. These by-product gas streams are the raw materials for carbon dioxide production. Two variations of the purification process for carbon dioxide manufacture are given in Figure 5-7. Permanganate scrubbing is used where elimination of organic impurities by oxidation is required. With relatively pure gas streams the standard process involves separation of "knockout" water (drying) as the primary purification step. Neither process produces any hazardous wastes for disposal on land. The typical plant has a 250 ton per day capacity and is 5 to 30 years old.

5.3.3 Elemental Gases and Other Industrial Gases (SIC 28134)

5.3.3.1 Helium

Helium is extracted cryogenically as a by-product of natural gas production. Many plants are owned and operated by the U.S. Bureau of Mines. There are no hazardous wastes attributable to the production, the flow diagram for the usual helium operation is given in Figure 5-8. Natural gas is cooled, liquified and rectified to separate the helium, which is then purified as shown.

The typical plant is located near a natural gas well in the Texas-Oklahoma area. Total production is small and, for the typical plant, is less than 10 tons per day. Practically all facilities are post World War II (30 years or less).

5.3.3.2 Air Distillation Products

The principal products produced from air distillation are oxygen and nitrogen.

The rare gases argon, neon, xenon, and krypton are also obtained from the same process. The usual composition of air is shown below:

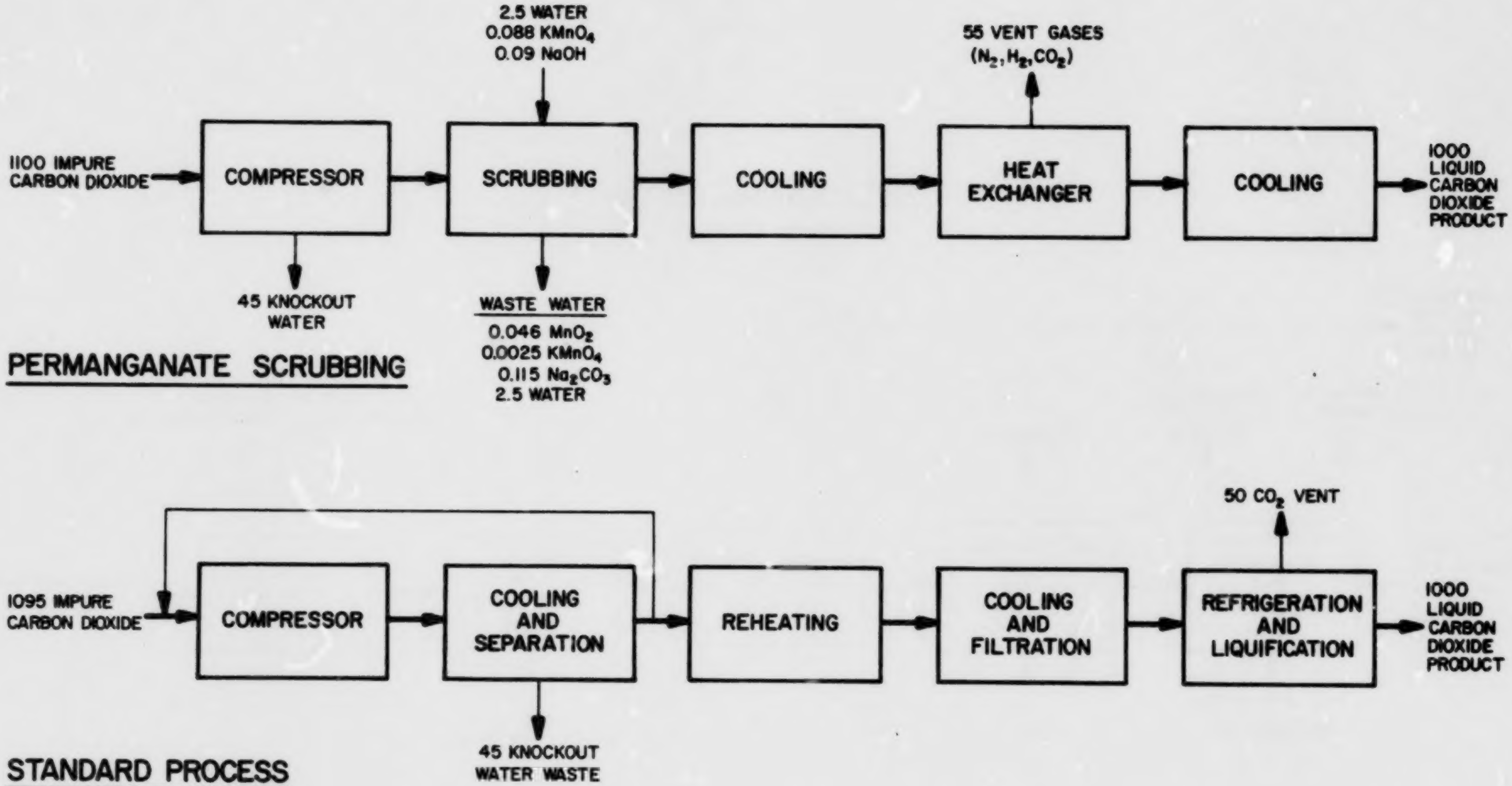

FIGURE 5-7
CARBON DIOXIDE MANUFACTURE

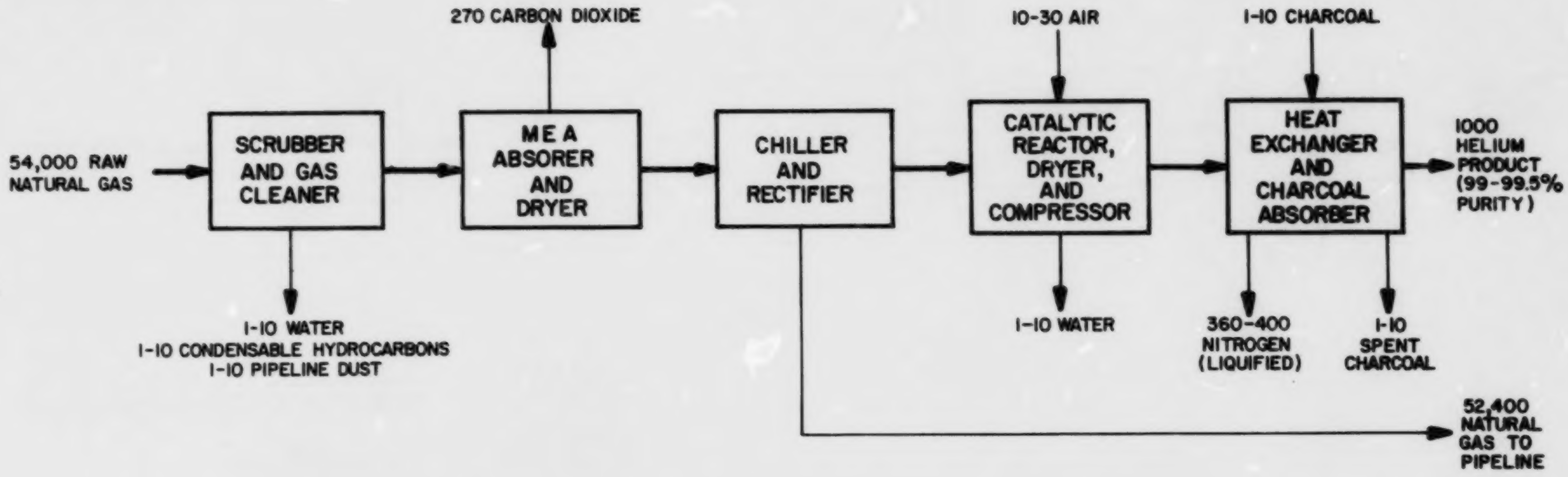
270 CARBON DIOXIDE
10-30 AIR
1-10 CHARCOAL
54,000 RAW NATURAL GAS
SCRUBBER AND GAS CLEANER
ME A ABSORER AND DRYER
CHILLER AND RECTIFIER
CATALYTIC REACTOR, DRYER, AND COMPRESSOR
HEAT EXCHANGER AND CHARCOAL ABSORBER
1000 HELIUM PRODUCT (99-99.5% PURITY)
1-10 WATER
1-10 CONDENSABLE HYDROCARBONS
1-10 PIPELINE DUST
1-10 WATER
360-400 NITROGEN (LIQUIFIED)
1-10 SPENT CHARCOAL
52,400 NATURAL GAS TO PIPELINE

FIGURE 5-8
HELIUM MANUFACTURE

Gas	Volume Percent
Air	100
Nitrogen	78.03
Oxygen	20.99
Argon	0.94
Hydrogen (up to)	0.01
Neon	0.0015
Helium	0.0005
Krypton	0.00011
Xenon	0.000009
Carbon dioxide	0.03-0.07

The rare gases are separated by side rectification columns from takeoffs at various points in an air separation plant, as shown in Figure 5-9. The wastes involved are only oil and grease from cooling compression seals.

No hazardous wastes are generated by these processes. The typical plant has a 500 tons per day capacity and is less than 30 years old.

5.3.3.3 Carbon Monoxide

Carbon monoxide is made by reforming methane with steam. The currently typical operation is shown in Figure 5-10. Hydrogen is a by-product, and there are no significant wastes produced. One plant accounts for about half of the U.S. production and the rest are small (about 50 tons per day). These plants are 5 to 30 years old.

5.3.3.4 Hydrogen

Hydrogen is produced as a co-product with carbon monoxide as shown in Figure 5-10, from natural gas by catalytic processes and by purification of refinery by-product gas. No significant amounts of wastes are generated in any case.

5.3.3.5 Nitrous Oxide

This gas is produced by thermal decomposition of ammonium nitrate followed by removal of co-product water vapor from the product gas stream. No hazardous wastes are generated and the flow diagram is given in Figure 5-11. The process reaction is:

$$NH_4NO_3 = N_2O + 2H_2O$$

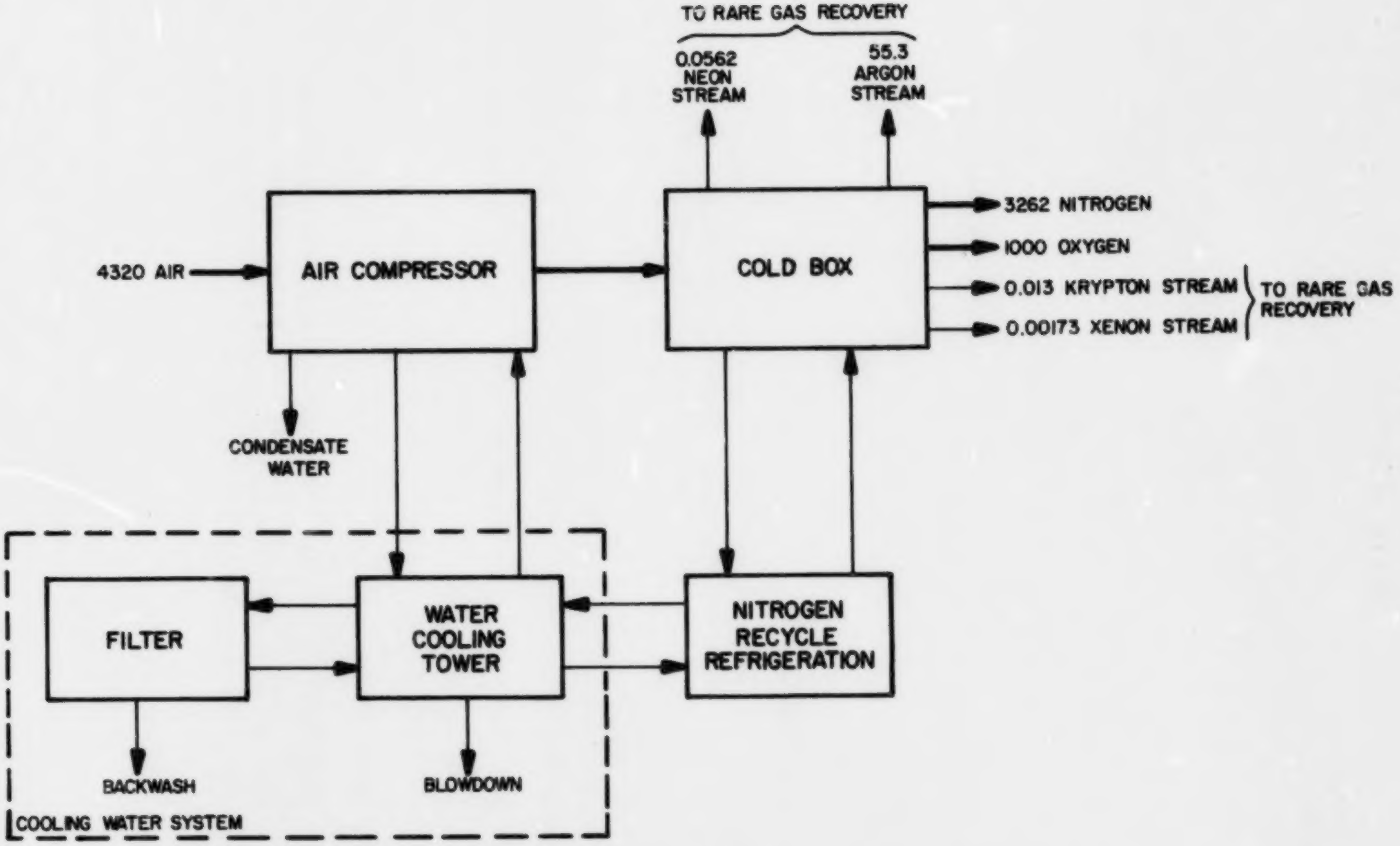

FIGURE 5-9
OXYGEN, NITROGEN AND RARE GASES MANUFACTURE

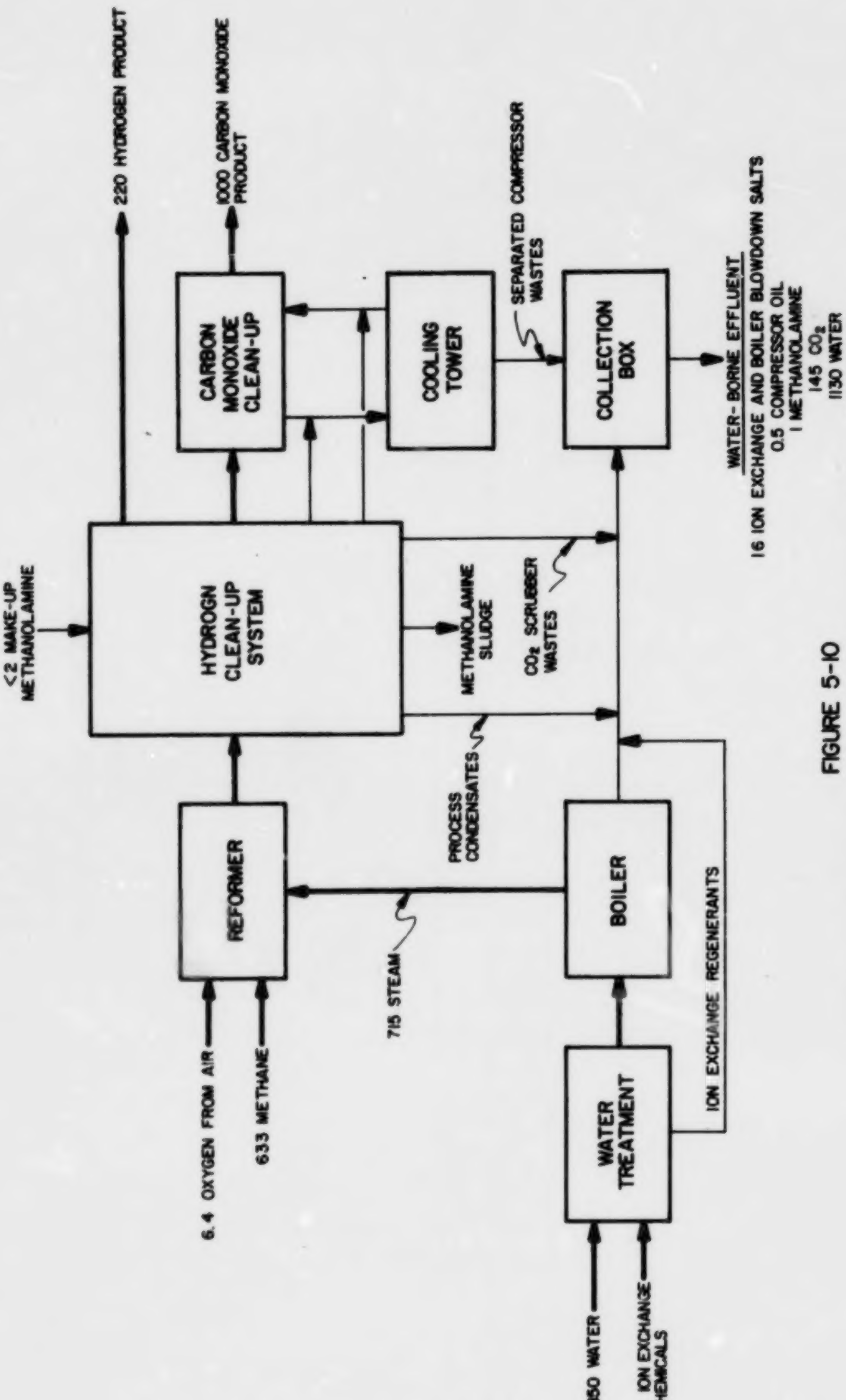

FIGURE 5-10

CARBON MONOXIDE AND HYDROGEN MANUFACTURE

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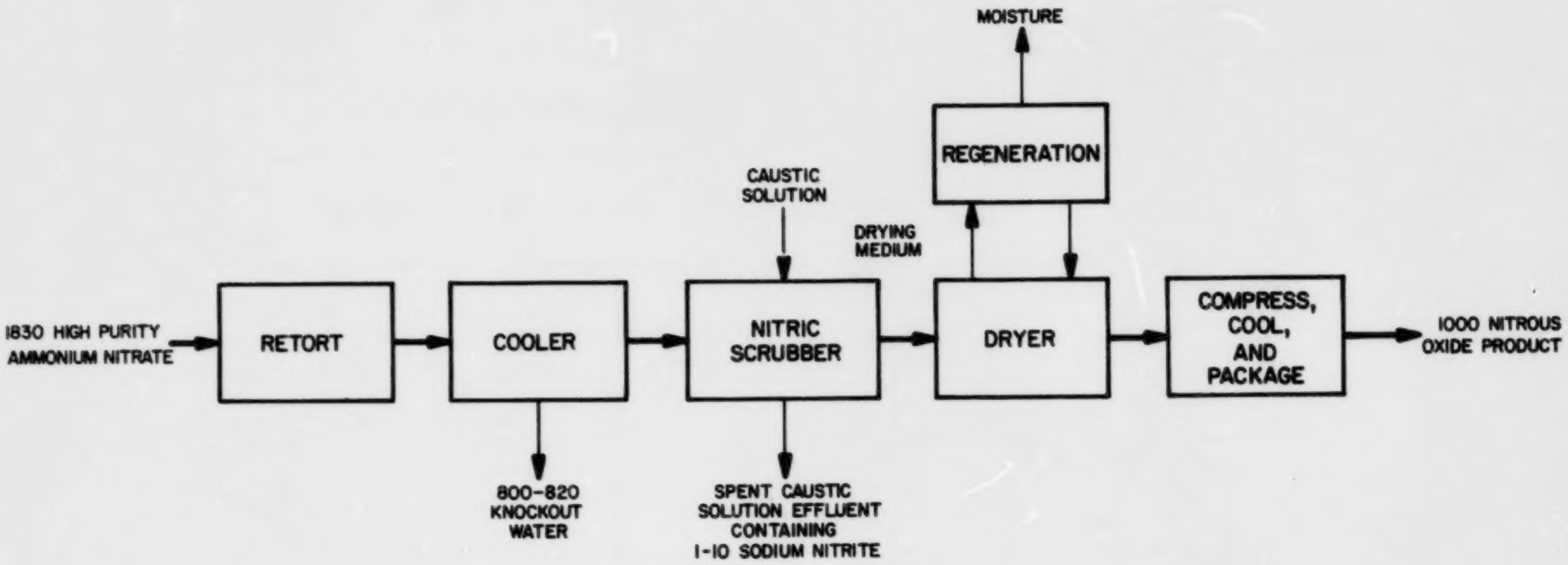

MOISTURE
REGENERATION
CAUSTIC SOLUTION
DRYING MEDIUM
1830 HIGH PURITY AMMONIUM NITRATE
RETORT
COOLER
NITRIC SCRUBBER
DRYER
COMPRESS, COOL, AND PACKAGE
1000 NITROUS OXIDE PRODUCT
800-820 KNOCKOUT WATER
SPENT CAUSTIC SOLUTION EFFLUENT CONTAINING 1-10 SODIUM NITRITE

FIGURE 5-11
NITROUS OXIDE MANUFACTURE

5.3.4 Aggregation of SIC 2813 Hazardous Wastes to Land Disposal

None of the processes producing the SIC 2813 industrial gases were found to generate hazardous wastes for land disposal.

5.3.5 Projection of SIC 2813 Hazardous Wastes to Land Disposal

No process change or impact of air or water regulations is expected to cause a significant generation of hazardous wastes for land disposal from the SIC 2813 category through 1983.

5.4 Inorganic Pigments (SIC 2816)

5.4.1 Introduction

This industry was subcategorized into three five-digit SIC industries; 28161 (Titanium Dioxide Pigments), 28162 (Other White Opaque Pigments), and 28163 (Chrome Colors and Other Inorganic Pigments).

The pigment products produced in each five-digit SIC subcatoregory are listed and discussed in Section 3 of this report. The purpose of the present section is to detail the processes by which the pigments are made, characterize the land destined wastes currently generated by the processes, and estimate the quantities of land destined waste expected from these processes in the years 1977 and 1983. The amounts of hazardous waste streams and the amount of hazardous constituents in them are presented on a state by state and EPA regional basis.

5.4.2 Titanium Dioxide Pigment (SIC 28161)

This material is generated by two processes - one involving the acidification of ilmenite ore in sulfuric acid and the other involving chlorination of rutile ore to produce $TiCl_4$ which is then converted to TiO_2. These processes will be discussed separately. Two facilities differ from the above generalizations in that they have the unique characteristic of simultaneously upgrading ilmenite ore and chlorination of the mineral, thus allowing use of a lower grade of ore than rutile with the chloride process.

5.4.2.1 Sulfate Process

In the sulfate process, titania-bearing ilmenite ores are dissolved in sulfuric acid to produce titanium sulfate as an intermediate product. The acid solution is clarified, a portion of the iron sulfates is removed by crystallization, and the titanium sulfate is hydrolyzed to form a white, non-pigmentary hydrate. The hydrate is calcined to form crystalline titanium dioxide, which is milled, surface treated, and packaged for sale. Product quality from the sulfate process is not so dependent on ore quality as is that from the chloride process.

A general reaction scheme for the sulfate process using ilmenite ore containing various iron oxides (FeO and Fe_2O_3) is as represented by the equations:

(a) acidification
$FeO(Fe_2O_3 \cdot TiO_2 + 5H_2SO_4 =$
$FeSO_4 + Fe_2(SO_4)_3 + TiOSO_4 + 5H_2O$

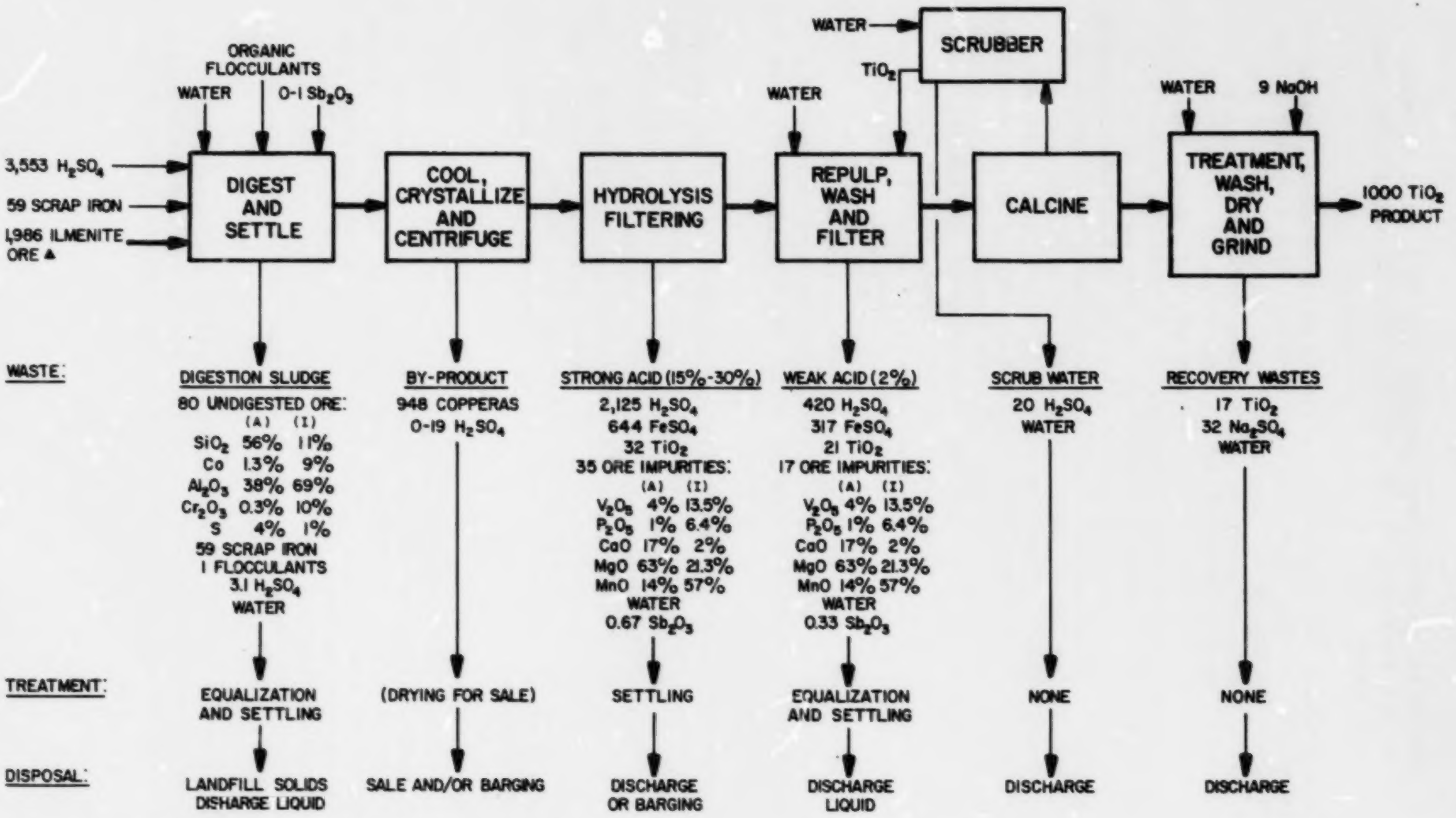
(b) hydrolysis to form hydrate
$TiOSO_4 + 2H_2O = TiO_2 \cdot 2H_2O + H_2SO_4$

(c) calcination
$TiO_2 \cdot 2H_2O + \text{Heat} = TiO_2 + H_2O$

A typical mass-balanced flow sheet for the manufacture of TiO_2 by the sulfate process is shown in Figure 5-12. There are two types of solid wastes produced by this process; ore residues and solids generated by wastewater treatment.

(a) Ore residues. In the sulfate process, ore residues consist of non-hazardous sulfuric acid insolubles such as silica, coke, and non-soluble ore impurities. The fact that impurities such as oxides of chromium and vanadium in the ore have not been dissolved by the strong acid treatment is direct evidence that they are not potentially hazardous upon land disposal, in the physical and chemical form that they have in the ore.

(b) Solids Generated by Wastewater Treatment. Plants which use the sulfate process which do not dispose of their acidic water-borne wastes by ocean dumping must, to meet future water quality standards, neutralize their wastewater effluents. This can be expected to generate large volumes of non-hazardous solid waste consisting of oxides and hydroxides of some of the water-borne ore impurities present in the ilmenite ore. The large solid waste loadings generated can be expected to



▲ *TYPICAL ORE IMPURITIES COMPOSITION:*

25-35% Al_2O_3	0-5% Co
5-35% SiO_2	4-28% MnO
10-27% MgO	2-7% V_2O_5
0-6% Cr_2O_3	

FIGURE 5-12
TITANIUM DIOXIDE MANUFACTURE BY THE SULFATE PROCESS

contain mostly iron oxides (or hydroxides) with trace amounts of the hydroxides of manganese and chromium.

Assuming neutralization will be by lime treatment, calcium sulfate would be the major precipitate. The concentration of trivalent chromium in the resultant sludge solids is estimated to vary between 0 to 185 ppm (w/w dry basis). This material would be present in the form of insoluble Cr_2O_3. Considering the large amount of the water that would probably be in the sludge (approx. 75 percent), the overall concentration of trivalent chromium in the waste would be less than 40 ppm. Lime precipitation of dissolved vanadium salts probably would form vanadate compounds and would be inefficient in removing dissolved vanadium since such compounds are fairly soluble in the water-borne effluent. Therefore, it is assumed that virtually no calcium vanadate will be precipitated, and most of the trace amounts of the vanadium present will be in the water-borne effluent. Thus the only potentially hazardous constituent of the TiO_2 sulfate process sludge from wastewater treatment would be trivalent chromium hydroxide in trace amounts. Antimony trioxide is not considered in these figures since its use is optional and its presence is not representative of the entire industry. Calcium sulfate, ferric hydroxide, and titanium dioxide would comprise over 99.9 percent of the dry waste stream.

The concentration of potentially hazardous constituents in the sulfate process waste stream destined for land disposal would then average less than 0.004 percent. The physical, chemical, biological, and environmental properties of trivalent chromium hydroxide is detailed in Appendix A. The concentration of chromium in this waste stream is such that the overall toxicological properties of the waste are reduced in comparison to a highly concentrated chromium containing waste.

There are several factors which were considered; the first being the ease of solubilization upon land disposal. The gradual percolation of water from the top to the bottom of a land disposed waste maximizes the potential for equilibrium saturation of the water. Upon exiting from the waste, the leachate should be saturated with waste component. The expected concentration of $Cr(OH)_3.nH_2O$ may be as much as 50mg/l at pH 5.5, because the dissolved $CaSO_4$ will maintain the leachate at this pH value.

A second factor is surface solubilization and erosion resulting in surface runoff. This factor varies depending upon the degree of protection the waste material has from wind and rain. Because of the sizeable quantities which may be generated by neutralization of TiO_2 water-borne waste streams, the effects of no protection are discussed. Surface solubilization of waste constituents is again pH dependent, but now the length of contact time between the waste and the water is much shorter. Therefore, a saturation concentration would not be expected for Cr, and the amount of dissolved hazardous material should not be environmentally significant. Chromium in the surface runoff from the precipitated TiO_2 water-borne waste stream will have no greater affect on the surrounding environment than that caused by other constituents, e.g. $CaSO_4$ with its greater solubility.

In summary, the precipitates from TiO_2 sulfate process wastewater neutralization will contain a small amount of hazardous constituents. However, the dilution factors of the other waste constituents minimizes the danger of environmental contamination due to these hazardous constituents. Thus it was concluded that little if any hazardous wastes destined for land disposal is currently generated by the sulfate process for the manufacture of TiO_2 pigment. Also, in the light of the foregoing discussion and the fact that no new sulfate process plants are planned for the foreseeable future, this situation should not experience any significant change through 1983.

5.4.2.2 Chloride Process

In the chloride process, titanium (TiO_2) ores are chlorinated to produce titanium tetrachloride as an intermediate. One manufacturer has a proprietary process at two plants which can use low grade ore (about 65 percent TiO_2) but the other manufacturers using the chloride process use rutile ore which is about 95 percent TiO_2 . The upgrading process to convert ilmenite (65 percent TiO_2) to rutile (95 percent TiO_2) mainly removes iron oxides from the ore. These two facilities generate one hundred times the waste load of pollutants generated by conventional chloride processes, as stated by the manufacturer. This is the result of the simultaneous, on-site beneficiation of low grade ore that takes place.

Coke is included to promote the reaction of the ore to titanium tetrachloride, which is then oxidized to titanium dioxide and chloride (which is recycled). A general reaction scheme using ileminte as the raw material is shown below:

(a) Chlorination reaction
$TiO_2 \cdot (Fe_2O_3) + 2Cl_2 + C = TiCl_4 + CO_2 + (FeCl_3)$

(b) Oxidation reaction
$TiCl_4 + O_2 = TiO_2 + 2Cl_2$

The chlorination reaction above is only approximate because the iron chloride which results may be a mixture of several chlorides, and some carbon monoxide is formed as well. The actual products and product ratios will depend on the raw material and the reactant ratios used.

Impurities in the system including the iron and other metals (Al, V, etc.), chlorides, entrained coke and ore, carbon monoxide and dioxide, and hydrogen chloride (HCl) all have to be removed prior to the oxidation reaction, which creates significant effluent waste control problems. After chlorination, the products are cooled to condense the undesired metal chlorides. Solids are separated by centrifugation or filtration, and the gaseous titanium tetrachloride is condensed. A number of techniques are used to further purify the tetrachloride.

After purification, the titanium tectrachloride is vaporized and passed into a reactor with heated air or oxygen. The solid titanium dioxide particles are mechanically separated from the gas stream, calcined, ground, surface-treated, and packed.

Figure 5-13 shows a typical mass-balanced flow sheet for the manufacture of TiO_2 by the chloride process using both types of ore.

As in the sulfate process, the chloride process yields two types of solid waste; ore residues and solids generated by wastewater treatment.

(a) Ore residues
In the case of the chloride process, the residues from initial chlorination consist of non-hazardous, non-solubilized ore residues resistant to strenous chlorination (e.g. carbon, and unreacted ore and a number of non-volatile chlorides of metallic impurities in the ore such as, $FeCl_3$). Land disposal of these solid materials requires no special precaution to guard against environmental contamination. The fact that these metallic impurities have not been reacted and altered in chemical form by the harsh chlorination process is direct evidence that they are not hazardous upon land disposal in this form. The non-volatile

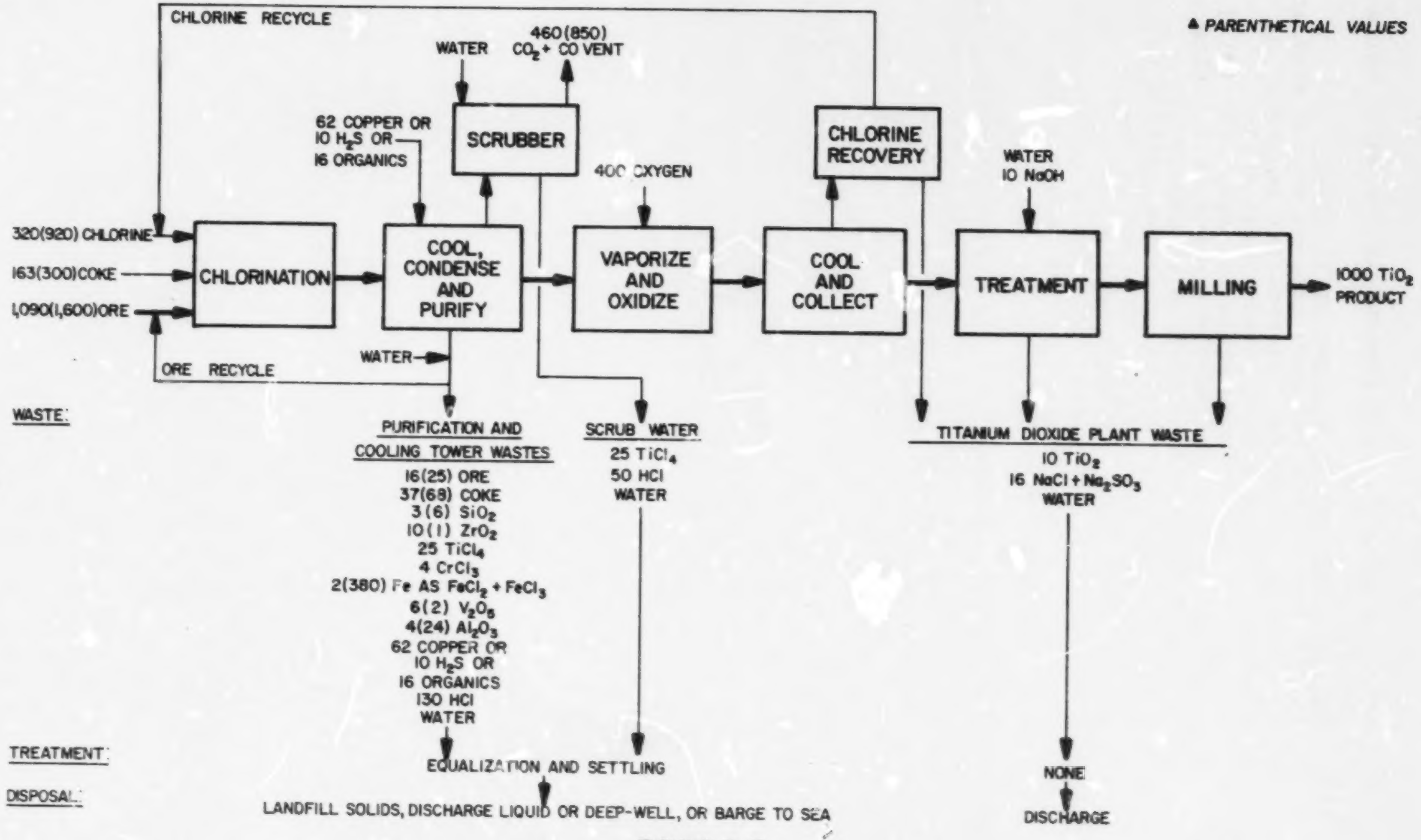


FIGURE 5-13
TITANIUM DIOXIDE MANUFACTURE
BY THE CHLORIDE PROCESS USING 95% ORE OR 65% ORE ▲

metallic chlorides are present in the water-borne effluent.

(b) Solids Generated by Wastewater Treatment

In the case of the chloride process wastes similar to those in the sulfate process are generated by treatment of the acidic, heavy metal salt-containing, water-borne waste streams. The solid waste can be expected to contain mostly titanium hydroxide and small amounts of compounds of vanadium, aluminum, copper, chromium, zirconium, and niobium. Where copper is added in the purification stage, it will be the major constituent in the waste. The use of copper is not considered representative of the industry and is not discussed here.

Assuming wastewater treatment is by lime neutralization, the following possibly hazardous constituents will be present in the resultant slurry: chromium, zirconium, vanadium and niobium. The properties of these elements and their compounds are detailed in Appendix A of this report. The most hazardous constituent is chromium, which comprises about 3 percent of the dry waste (1 percent on a wet weight basis). This is sufficiently concentrated that the overall biological properties of the wastes are very similar to those of the individual constituents, and stringent precautions will be necessary to protect surface and ground waters upon land disposal. The concentrations and forms of the other three metallic materials listed above are not judged to be hazardous.

There are six chloride process and five sulfate process plants. The typical plant produces 300 tons per day and is 5 to 30 years old. Production growth in this subcategory is expected to take place only in those geographic locations presently producing titanium dioxide. No new sulfate process plants are expected to be built. New capacity installation will be solely in the chloride process and will accompany technological developments to upgrade ilmenite ore to be compatible with the chloride process.(70) The principal impact of air and water regulations will be to cause more of these heavy metal constituents of the acid waste streams to be precipitated for land disposal or for deep-welling or barging, depending upon regulations operational in these areas.

5.4.2.3 Aggregation of SIC 28161 Hazardous Wastes to Land Disposal

The amounts of the constituents of the waste streams containing hazardous materials in sufficient quantities to be hazardous in total are shown for the typical or usual operation in the flow diagrams in the preceding sections. The values given are relative to the product rate, that is, they are numerically equivalent to either kilograms per metric ton of product or pounds per 1000 pounds of product. The hazardous waste streams from this industry subcategory are all from the chloride process and consist of chromium compounds generated by process wastewater treatment.

The amount of water in these waste streams can be expected to vary from 30-60 percent depending on the dewatering method employed.

The Table 5-4 lists the aggregate hazardous waste streams of SIC 28161 on a state-by-state, regional, and total U.S. basis, and the amounts of the hazardous constituents estimated to be currently valid. This table also includes projections of waste quantities take expected in the years 1977 and 1983. The local situation in each state (where deviations from the "typical" occurs are taken into account insofar as is possible.

The data in this table is a mixture of the most reliable and the more consistent entries from three sources:

- -calculated from consistent manufacturers' data
- -estimated from fragmentary or equivocal manufacturers' data
- -our own estimates

The hazardous constituent (chromium) is given in terms of the amount of the chemical element since the hazardous nature of this material is specific to the chemical element whether or not it is in elementary or combined form in the waste stream. Thus the only waste stream destined for land disposal considered to be potentially hazardous in SIC 28161 is the solid fraction of the treated wastewater stream from the chloride process, and this only because of its chromium content. The table gives the total amount of wastes in the stream and also the amount of the hazardous constituent on a dry basis.

The total of the waste stream in the U.S. currently amounts to 151,000 metric tons per year with the hazardous chromium constituent comprising 348 metric tons per year. These wastes occur in EPA regions III, IV, V, and IX, with region

Table 5-4. Hazardous Wastes Destined for Land Disposal Generated by Industry Subcategory 28161, Titanium Pigments (metric tons per year, dry basis)

		Current		1977		1983	
		Chromium Content	Total Hazardous Waste	Chromium Content	Total Hazardous Waste	Chromium Content	Total Hazardous Waste
IV	Alabama						
X	Alaska						
IX	Arizona						
VI	Arkansas						
IX	California	28	17,000	38	23,000	49	30,000
VIII	Colorado						
I	Connecticut						
III	Delaware						
IV	Florida						
IV	Georgia	42	10,000	82	19,000	131	30,000
IX	Hawaii						
X	Idaho						
V	Illinois						
V	Indiana						
VII	Iowa						
VII	Kansas						
IV	Kentucky						
VI	Louisiana						
I	Maine						
III	Maryland	26	6,000	55	13,000	89	21,000
I	Massachusetts						
V	Michigan						
V	Minnesota						
IV	Mississippi	46	11,000	62	14,000	82	19,000
VII	Missouri			39	9,000	86	20,000
VIII	Montana						
VII	Nebraska						
IX	Nevada						
I	New Hampshire						
II	New Jersey						
VI	New Mexico						
II	New York						
IV	North Carolina						
VIII	North Dakota						
V	Ohio	56	13,000	76	17,000	99	23,000
VI	Oklahoma						
X	Oregon						
III	Pennsylvania						
I	Rhode Island						
IV	South Carolina						
VIII	South Dakota						
IV	Tennessee	150	94,000	210	127,000	270	167,000
VI	Texas						
VIII	Utah						
I	Vermont						
III	Virginia						
X	Washington						
III	West Virginia						
V	Wisconsin						
VIII	Wyoming						
TOTAL		350	150,000	560	220,000	810	310,000
Region	I						
	II						
	III	26	6,000	55	13,000	89	21,000
	IV	240	115,000	350	160,000	480	220,000
	V	56	13,000	76	17,000	99	23,000
	VI						
	VII			39	9,000	86	20,000
	VIII						
	IX	28	17,000	38	23,000	44	30,000
	X						

IV having about 75 percent of the total. The wastes from the one plant that barges its wastes to sea were not included in the table since it is not land disposed. Approximately 60 percent of the total waste streams is disposed of by deep welling while most of the remainder is sent to settling ponds. It would therefore be very difficult to estimate the exact amount of water present in these waste streams although a range of from 30-80 percent water is estimated. The amount of hazardous waste stream barged to sea at present is estimated to be 36,000 metric tons per year (dry basis) from a chloride process plant in Delaware (Region III).

5.4.2.4 Projection of SIC 28161 Land Destined Hazardous Wastes to 1977 and 1983

The following assumptions were made in predicting the amounts of hazardous wastes destined for land disposal arising from the titanium pigment industry in the years 1977 and 1983:

- no new sulfate process plants will be built,
- all growth in this industry will take place in those states now having TiO_2 production,
- all chloride process plants will grow proportionally at a rate of 3 percent per year,
- the one chloride process plant using ocean barging will continue to do so, and
- implementation of 1977 and 1983 water effluent guidelines will not add significant quantities of hazardous constituents to the solids destined for land disposal.

Table 5-4 also lists the projections for 1977 and 1983 land destined hazardous waste streams from the chloride process for the manufacture of titanium pigment using the assumptions noted above.

The trend of total amounts of hazardous waste streams and hazardous constituent on a dry basis in metric tons per year projected for SIC 28161 are summarized as follows:

Period	Current	1977	1983
Chromium constituent	350	560	800
Total waste stream	151,000	222,000	310,000

Whereas about two-thirds of the present production of titanium pigment is manufactured by the sulfate process, it is expected that, by 1983, two-thirds of this pigment's production will be made by the chloride process.

Various grades, purities, and surface finishes in several crystalline forms are sold commercially. The pigment is also sold mixed with 50 to 70 percent calcium sulfate. Although the paint industry is the major user, various types of titanium dioxide are used in paper, inks, fabrics, rubber, and floor coverings. Total U.S. production in 1972 was 639,700 metric tons (705,300 tons). Domestic ore is found in New York and Florida, plus lesser amounts in North Carolina, Virginia, and Idaho. The remaining ore supply is imported, much of it from Canada and India. Most of the production of this pigment is captive to the large paint manufacturers.

5.4.3 Other White Opaque Pigments (SIC 28162)

This five-digit SIC subcategory includes the pigments, lead sulfates, lead carbonates, zinc oxide, antimony oxide, and lithopone (coprecipitated barium sulfate and zinc sulfide). Although these pigments contain very hazardous constituents, this industry group yields very small amounts of hazardous waste that is destined for land disposal. Because of their value, practically all of the waste streams containing lead, zinc, and antimony are recovered and either recycled back to the process or sold to recover metal values.

5.4.3.1 Lead Sulfates (White Lead)

Normal lead sulfate ($PbSO_4$) is prepared by reaction of dilute sulfuric acid with lead acetate solutions. The product is recovered by filtration. Basic lead sulfate ($PbSO_4 \cdot PbO$) is prepared by several methods:

(a) by flash roasting of the finely divided lead sulfide;
(b) by reaction of lead, sulfur dioxide, and oxygen and in special furnaces
(c) by reaction of litharge (PbO) with dilute sulfuric acid and the product recovered by filtration.

A mass-balanced flow sheet showing the manufacture of basic lead sulfate by a dry process and the manufacture of normal lead sulfate by a wet process appears as Figure 5-14. For those processes involving furnace oxidations, all wastes are air-borne and are generally recovered by bag filtration methods and recycled. For the aqueous processess, treatment of water-borne waste streams with base or sulfide generates small amounts of insoluble lead salts, which are generally

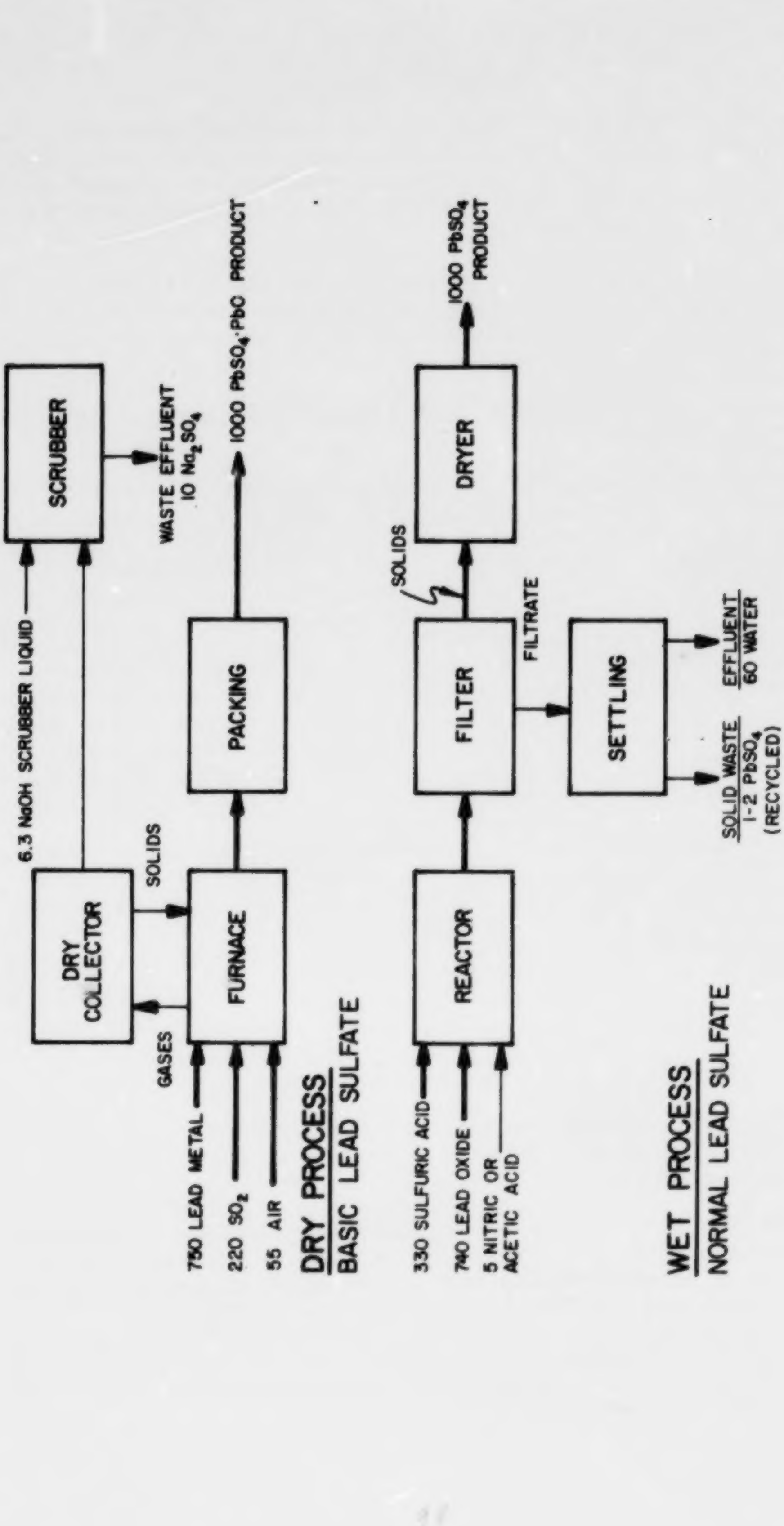


FIGURE 5-14
LEAD SULFATE MANUFACTURE

recycled. The waste lead sludge could be hazardous, and if the waste was not recycled, disposal on land would require stringent safeguards to protect surface and ground waters. The properties of lead sulfate and lead hydroxide are described in Appendix A.

One company produces the majority of this material in four states across the country. Plants are relatively small (ca. 10 tons per day) and generally occur as part of paint manufacturing complexes.

5.4.3.2 Lead Carbonate, Lead Basic Carbonate (also White Lead)

Normal lead carbonate is prepared either by reaction of lead acetate solutions with CO_2 or by reaction of this same material in solution with ammonium carbonate. The product is recovered by filtration. Basic lead carbonate is prepared by partial calcination of the normal material. All wastes are airborne (in the form of dusts) and are generally removed from vent gases by bag collection methods and recycled. Treatment of water-borne wastes from the normal carbonate manufacture generates small amounts of insoluble lead salts as solid wastes and these are generally recycled. The same remarks about lead sulfate production apply to the lead carbonates. Figure 5-15 show a typical mass-balanced flow sheet for the manufacture of lead carbonate.

The precipitated lead salt waste resulting from treatment of wastewater effluents could be hazardous. If the waste was not recycled, disposal on land would require stringent safequards to protect surface and groundwaters. The properties of lead carbonate, basic lead carbonate, and lead hydroxide are discussed in Appendix A.

5.4.3.3 Zinc Oxide

This material is made by two processes:

(a) those involving oxidation of zinc, and
(b) those involving precipitation from solution followed by calcination.

In the first case, all solid wastes produced are either in the form of furnace slags or as dusts. Contacts with several producers using the first type of processes have shown that all of the flue dusts are collected by dry collection methods and sold or reprocessed for their lead and cadmium content. The various slags produced are also generally utilized to recover residual zinc. There are no other wastes involved.

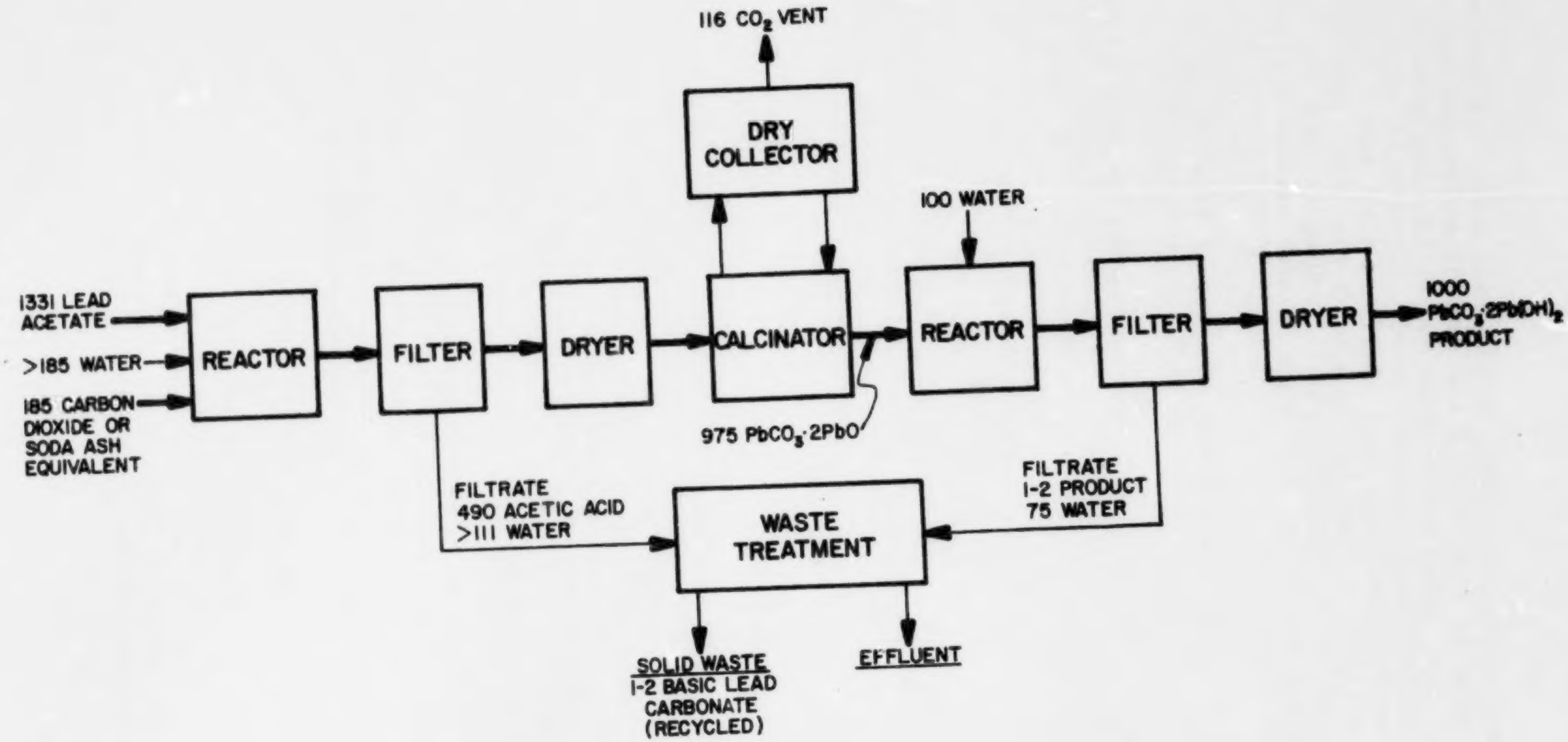


FIGURE 5-15
LEAD CARBONATE MANUFACTURE

In the wet type processes, crude zinc oxide is leached with caustic soda to remove sulfate and dissolve the lead salts present. The undissolved zinc oxide is then recovered, washed, neutralized, and calcined. Treatment of the waste aqueous caustic streams with barium salts and sulfides removes sulfate (as $BaSO_4$) and lead (as PbS) from the effluent prior to neutralization. Most of the PbS generated is recovered and sold, and some of the barium sulfate is also recovered.

Figure 5-16 is a typical mass-balanced flow sheet for the manufacture of zinc oxide by the thermal oxidation process.

The solid wastes from zinc oxide production are composed of barium sulfate, lead sulfide, cadmium residues. The lead and cadmium compounds could be hazardous, but they are recovered to reclaim heavy metal values. The properties of zinc oxide, lead sulfate and cadmium are detailed in Appendix A.

This chemical is made throughout the United States. Largest production occurs in Kansas and Pennsylvania. The typical plant is not easily quantified, since there are a number of relatively large plants, these latter averaging from 30 to 120 tons per day.

5.4.3.4 Lithopone

Lithopone is produced by reaction of barium sulfide and zinc sulfate solutions. The product, a mixture of $BaSO_4$ and ZnS, both of which are insoluble, is recovered by filtration. There are no hazardous land-destined wastes generated from this process, and no mass-balanced flow sheet is presented to avoid disclosure of process details of the one U.S. manufacturer."

5.4.3.5 Zinc Sulfide

Pure zinc sulfide is also categorized by the U. S. Census as being a part of the SIC 28162 industry. However, there is presently no pigment grade zinc sulfide production in the U.S. This pigment has been completely replaced by titanium dioxide because of cost and pigment quality.

5.4.3.6 Antimony Oxide

This material is prepared by an ore extraction process, wherein the ore is first dissolved in sulfuric acid and the antimonyl sulfate formed then converted to product Sb_2O_3. A typical mass-balanced flow sheet appears as Figure 5-17. The solid wastes generated by the process are of three types:

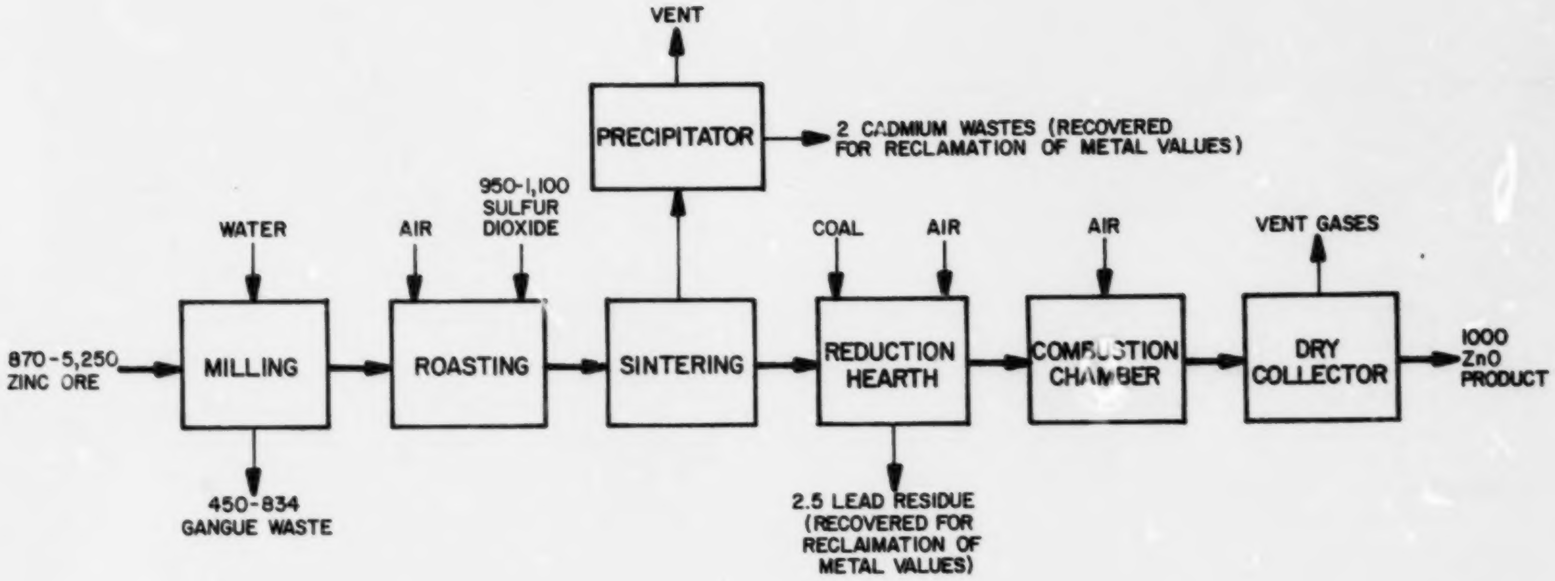
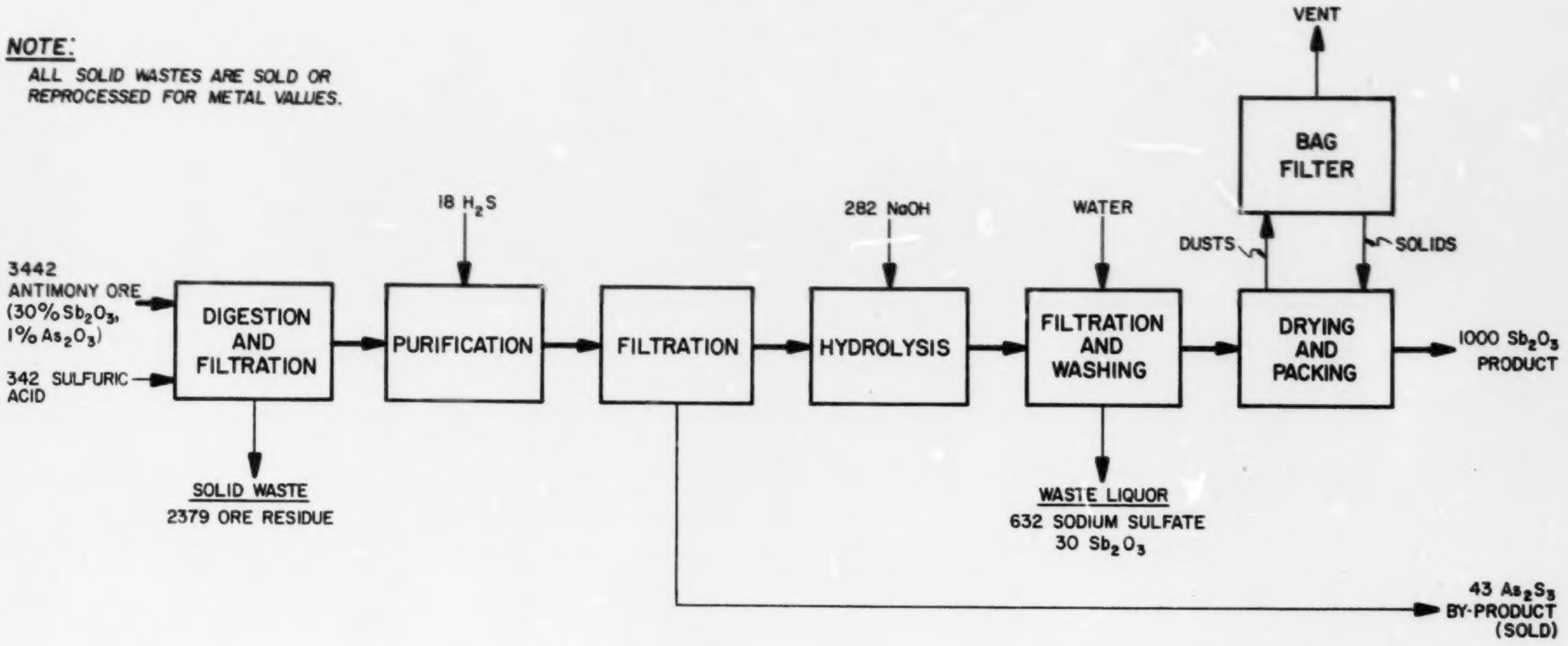


FIGURE 5-16
ZINC OXIDE MANUFACTURE
BY THE THERMAL OXIDATION PROCESS



NOTE:
ALL SOLID WASTES ARE SOLD OR REPROCESSED FOR METAL VALUES.

FIGURE 5-17
ANTIMONY OXIDE MANUFACTURE

(a) Ore residues containing acid insoluble inert materials such as silica. These are non-hazardous.

(b) Various product purification sludges. These contain arsenic compounds; e.g., As_2S_3 in small amounts. Arsenic sulfide is a hazardous compound whose chemical, physical, and biological properties are described in Appendix A.

(c) A small antimony oxide waste results from solids removed during waste water treatment. Antimony compounds are potentially hazardous. The chemical, physical and biological properties of antimony trioxide are described in Appendix A.

Of the six plants in the U. S. producing antimony oxide, only one does not recover their solids wastes for reclamation of metal values. These plants are located in four states and are less than 30 years old. The present total production of antimony oxide in the U. S. is about 8000 metric tons per year.

5.4.3.7 Aggregate of SIC 28162 Hazardous Wastes to Land Disposal

Of all the hazardous wastes generated by this five-digit SIC industry, only one antimony oxide plant's waste is not recovered for reclamation of metal values. These wastes are listed in Table 5-5 and currently amount to 12 metric tons of antimony compounds per year and 0.24 metric tons of arsenic compounds per year on a dry basis. The total waste stream (including innocuous ore residue wastes) currently amounts to 240 metric tons per year on a dry basis. Because these wastes are mostly filter cake residues, the water content of the waste streams would probably range from 20 to 40 percent.

5.4.3.8 Projection of SIC 28162 Land Destined Hazardous Wastes to 1977 and 1983

The one antimony oxide plant accounting for the land-destined hazardous waste currently being generated by this industry is stockpiling the solids for possible future reclamation of metal values. Because specific plans have not been formulated along these lines, the projection of future amounts of wastes were based on a three percent per year growth pattern through 1983. Recommended effluent limitations guidelines will not add significant quantities of land-destined hazardous wastes to this industry subcategory. Table 5-5 also lists the amounts of land-destined hazardous waste projected for the years 1977 and 1983 provided the one plant generating these wastes does not recover them to reclaim metal values before this time.

Table 5-5. Hazardous Wastes Destined for Land Disposal Generated by Industry Subcategory 28162, Other White Pigments, Currently and Projected for the Years 1977 and 1983 (metric tons per year, dry basis)

		Current			1977			1983		
		Total Hazardous Waste	Antimony Compounds	Arsenic Compounds	Total Hazardous Waste	Antimony Compounds	Arsenic Compounds	Total Hazardous Waste	Antimony Compounds	Arsenic Waste
IV	Alabama									
X	Alaska									
IX	Arizona									
VI	Arkansas									
IX	California									
VIII	Colorado									
I	Connecticut									
III	Delaware									
IV	Florida									
IV	Georgia									
IX	Hawaii									
X	Idaho									
V	Illinois									
V	Indiana									
VII	Iowa									
VII	Kansas									
IV	Kentucky									
VI	Louisiana									
I	Maine									
III	Maryland									
I	Massachusetts									
V	Michigan									
V	Minnesota									
IV	Mississippi									
VII	Missouri									
VIII	Montana									
VII	Nebraska									
IX	Nevada									
I	New Hampshire									
II	New Jersey									
VI	New Mexico									
II	New York									
IV	North Carolina									
VIII	North Dakota									
V	Ohio	240	12	0.24	270	14	0.28	320	16	0.34
VI	Oklahoma									
X	Oregon									
III	Pennsylvania									
I	Rhode Island									
IV	South Carolina									
VIII	South Dakota									
IV	Tennessee									
VI	Texas									
VIII	Utah									
I	Vermont									
III	Virginia									
X	Washington									
III	West Virginia									
V	Wisconsin									
VIII	Wyoming									
TOTAL		240	12	0.24	270	14	0.28	320	16	0.34
Region I										
II										
III										
IV										
V		240	12	0.24	270	14	0.28	320	16	0.34
VI										
VII										
VIII										
IX										
X										

5.4.4 Chrome Colors and Other Inorganic Pigments (SIC 28163)

This industry subcategory includes two broad groupings of pigments; Chrome Colors and Other Inorganic Pigments. The chrome colors include chrome yellows and oranges, molybdate chrome orange, zinc yellow, anhydrous and hydrated chrome oxide greens, chrome green and iron blues (not a chrome pigment, but usually produced in chrome pigment complexes). The other inorganic pigments include barium sulfate, cadmium colors, colored lead pigments, cobalt colors, iron oxide pigments, carbon black, and mercury sulfide.

The manufacture of all pigments in the chrome color group generates hazardous wastes destined for land disposal. Only cadmium colors and mercury sulfide manufacture of the other inorganic pigment group contributes hazardous wastes destined for land.

5.4.4.1 Chrome Yellows and Oranges (Lead Chromate)

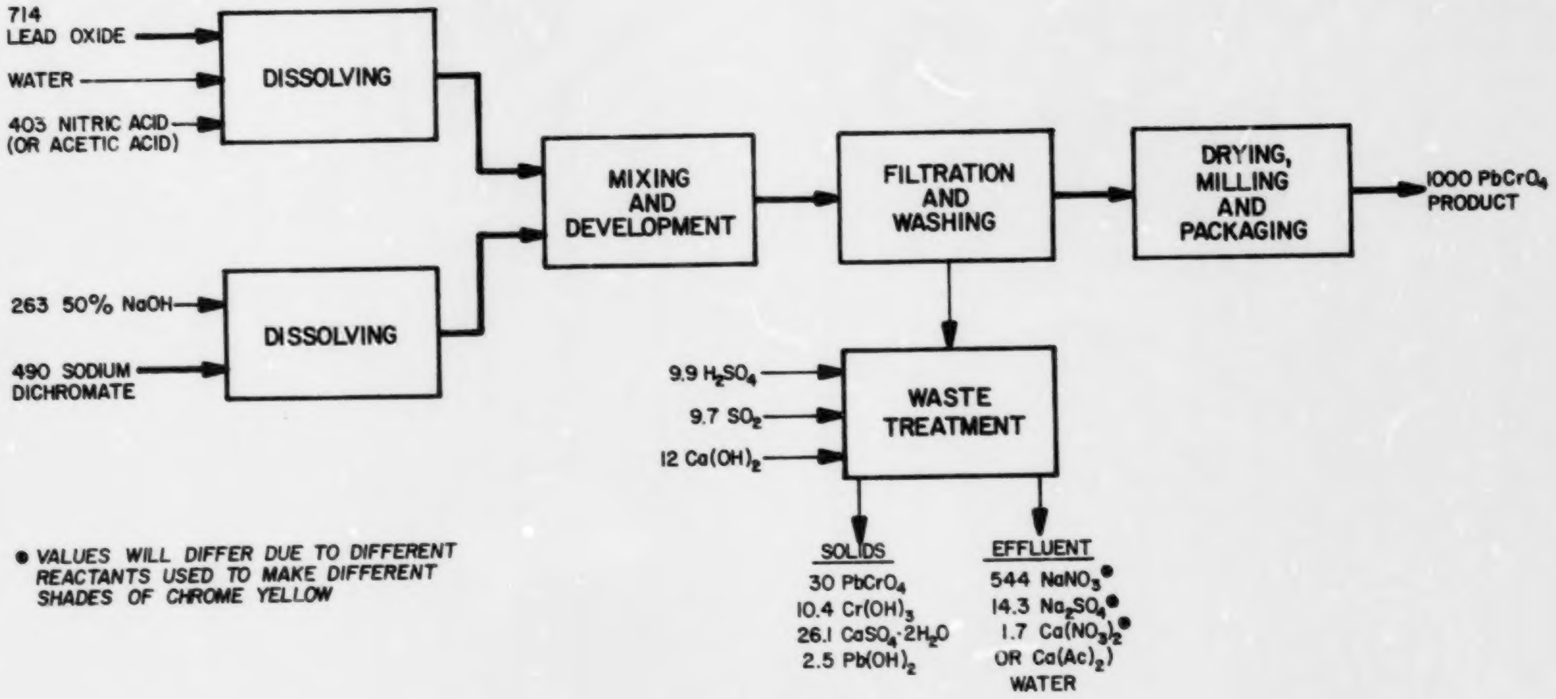
Chrome yellow is produced by reaction of sodium dichromate with a soluble lead salt. The product is recovered by filtration. Treatment of wastewaters generates a solid waste containing lead salts and chromium hydroxide. The properties of chromium hydroxide, lead hydroxide, and lead chromate are given in Appendix A.

A typical mass-balanced flow chart for the manufacture of lead chromate is shown in Figure 5-18. As indicated on the flow chart, the amounts and types of reactants and wastes will differ depending on the color being produced.

5.4.4.2 Molybdate Orange (Lead Molybdate Lead Chromate)

Molybdate orange is made by dissolving molybdic oxide in aqueous sodium hydroxide prior to the addition of sodium chromate. This solution is mixed and reacted with a solution of lead oxide in nitric acid. The reacting solution is then fed to a holding tank wherein the reaction goes to completion. The resulting suspension is filtered and the recovered product is washed, dried, milled and packaged.

The waste problems involved in the manufacture of molybdate orange are essentially the same as those for chrome yellow. Appendix A describes the properties of these waste constituents.



● VALUES WILL DIFFER DUE TO DIFFERENT REACTANTS USED TO MAKE DIFFERENT SHADES OF CHROME YELLOW

FIGURE 5-18
CHROME YELLOW MANUFACTURE

Figure 5-19 shows a typical mass-balanced flow sheet for the manufacture of molybdate orange.

5.4.4.3 Zinc Yellow

Zinc yellow is a hydrated zinc potassium chromate ($4ZnO \cdot K_2O \cdot 4CrO_3 \cdot 3H_2O$). It is usually made by the reaction of zinc oxide, hydrochloric acid, sodium dichromate and potassium chloride to give a zinc yellow slurry. This slurry is then filtered, washed, dried, milled and then packaged for sale. (See Figure 5-20)

Treatment of the waterborne wastes from the process generages insoluble zinc salts, chromium hydroxide, and unrecovered zinc yellow, all of which require careful disposal. The properties of zinc yellow, zinc oxide and chromic hydroxide are described in Appendix A.

5.4.4.4 Chrome Green

Chrome green is produced (as shown in Figure 5-21) by mixing a slurry of chrome yellow and iron blue. The slurry is washed, filtered, dried, ground, blended and packaged for sale. The waste problems are similar to those encountered tor the two individual constituent pigments, which become wastes to land disposal as the suspended pigment particles (chrome green) are removed in wastewater treatment. These compounds are described in Appendix A.

5.4.4.5 Chrome Oxide Green (Anhydrous and Hydrated)

Chrome oxide green is produced by two methods. The first, (for the anhydrous product) thermally reduces sodium dichromate with either sulfur or carbon or both. The recovered oxide material is then washed free of other compounds, dried, and packaged. The washwaters require treatment and this generates sludges of chromium compounds which require careful disposal. Figure 5-22 is a mass-balanced flow sheet for its manufacture. Appendix A describes the properties of chromic oxide and chromium hydroxide.

The second process produces a hydrated product. A mixture of boric acid and sodium dichromate is heated, the product is separated by filtration, washed, dried, and packaged. Treatment of wastewaters is required and this is expected to generate some chromium containing solids requiring disposal. Figure 5-23 describes this process, and the properties of the hazardous constituents are described in Appendix A.

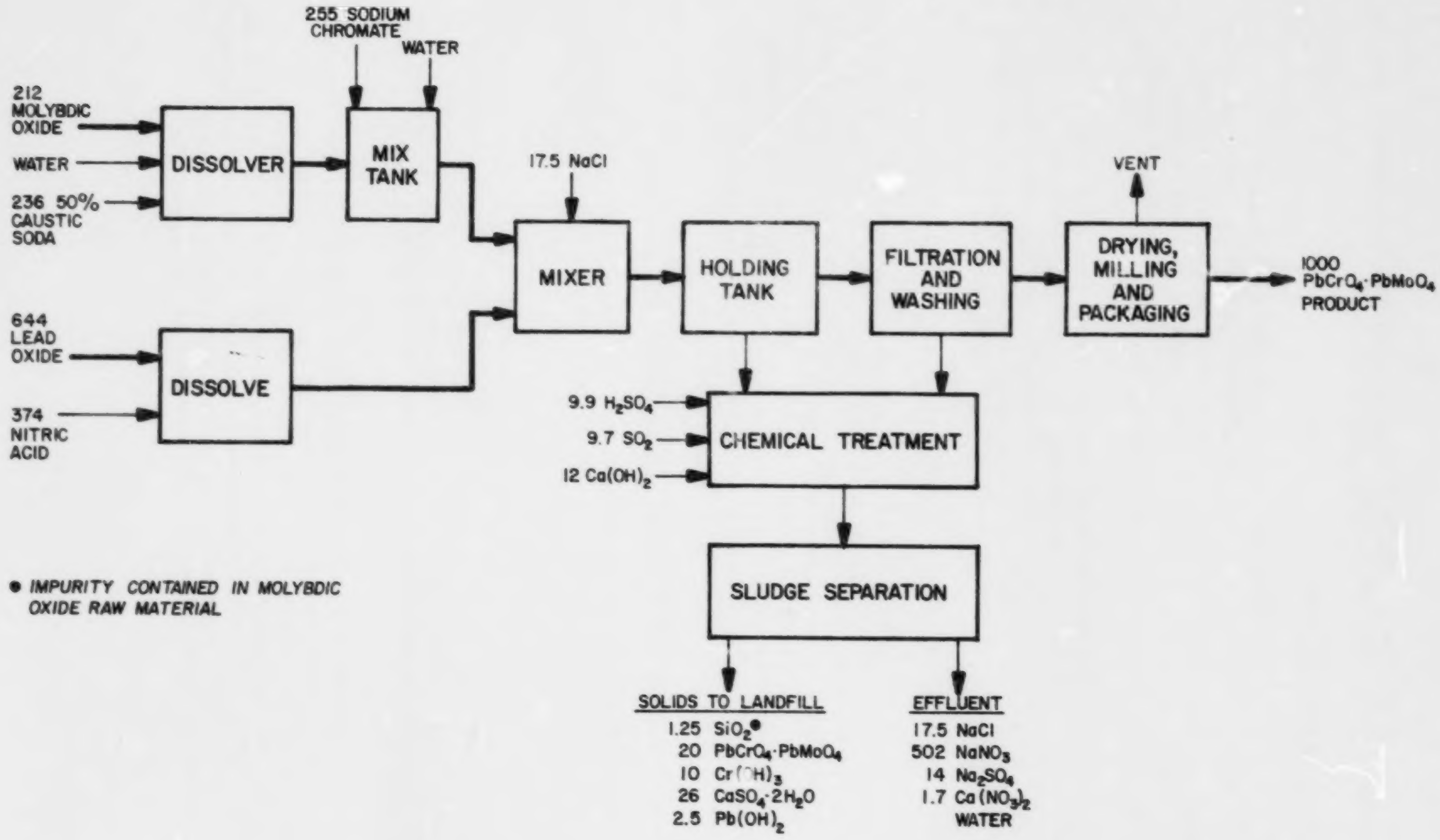


FIGURE 5-19
MOLYBDATE ORANGE MANUFACTURE

● IMPURITY CONTAINED IN MOLYBDIC OXIDE RAW MATERIAL

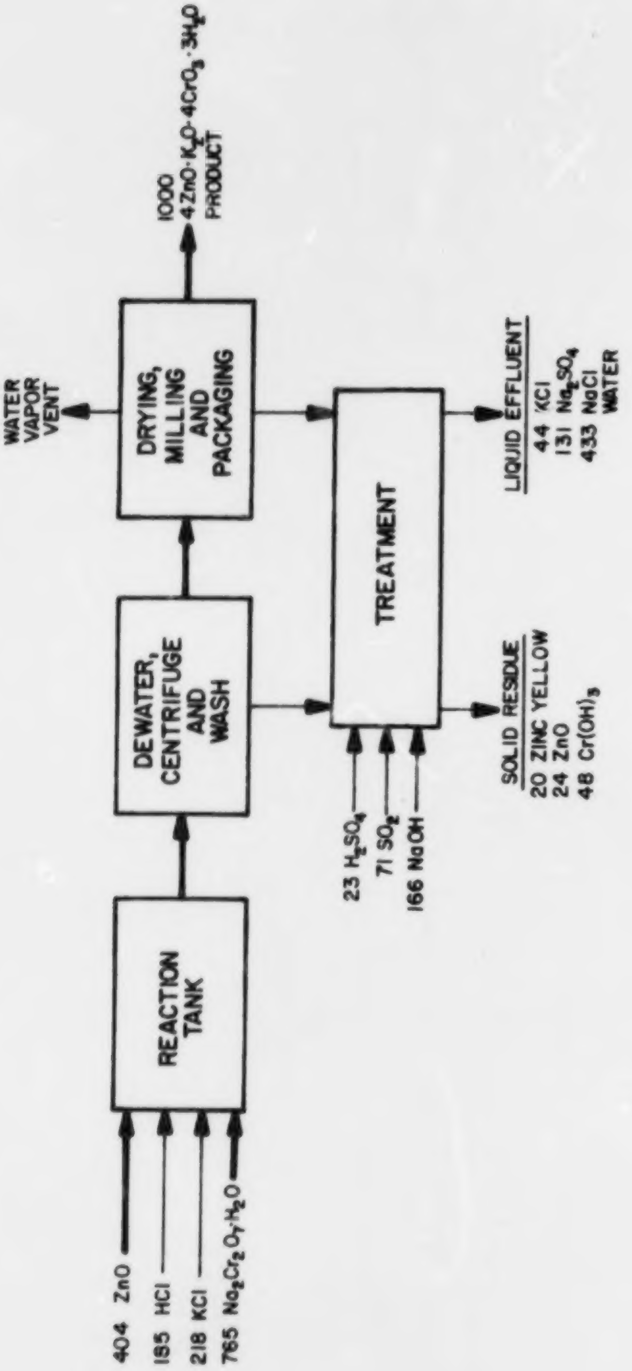
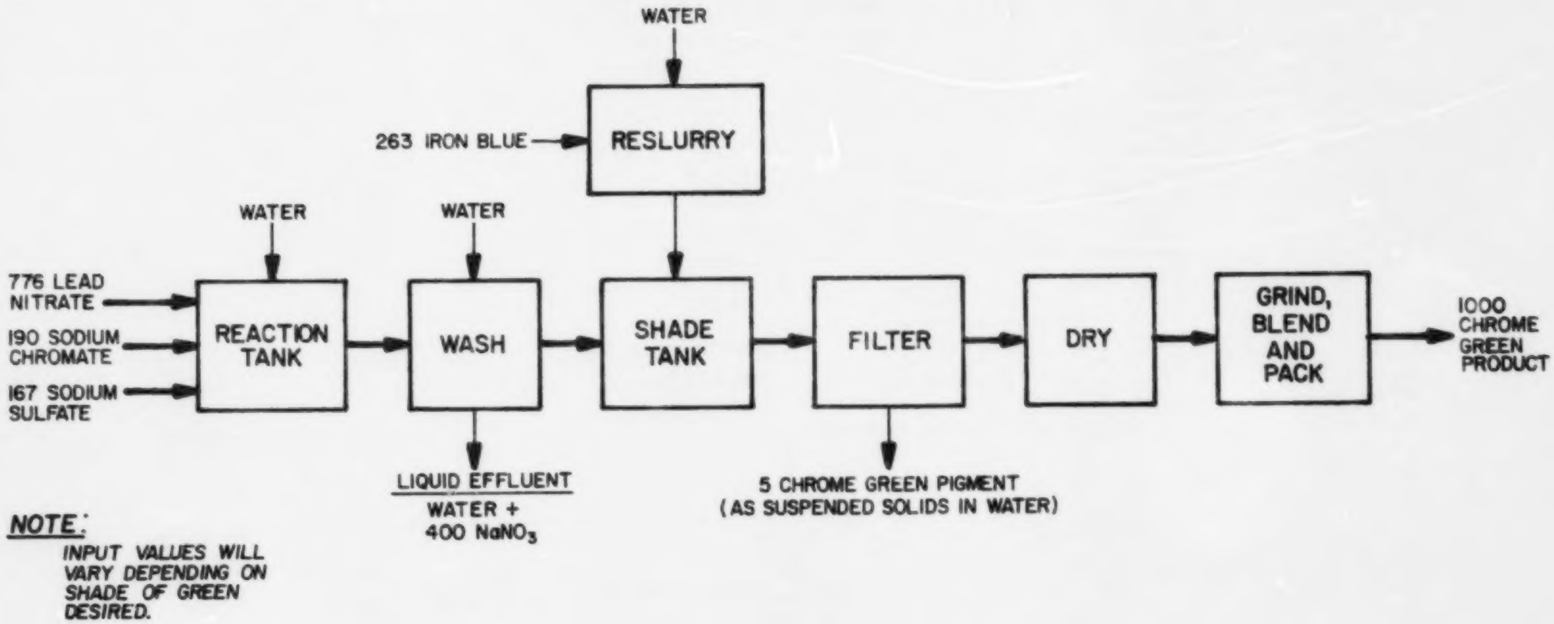


FIGURE 5-20
ZINC YELLOW MANUFACTURE



NOTE:
INPUT VALUES WILL VARY DEPENDING ON SHADE OF GREEN DESIRED.

FIGURE 5-21
CHROME GREEN MANUFACTURE

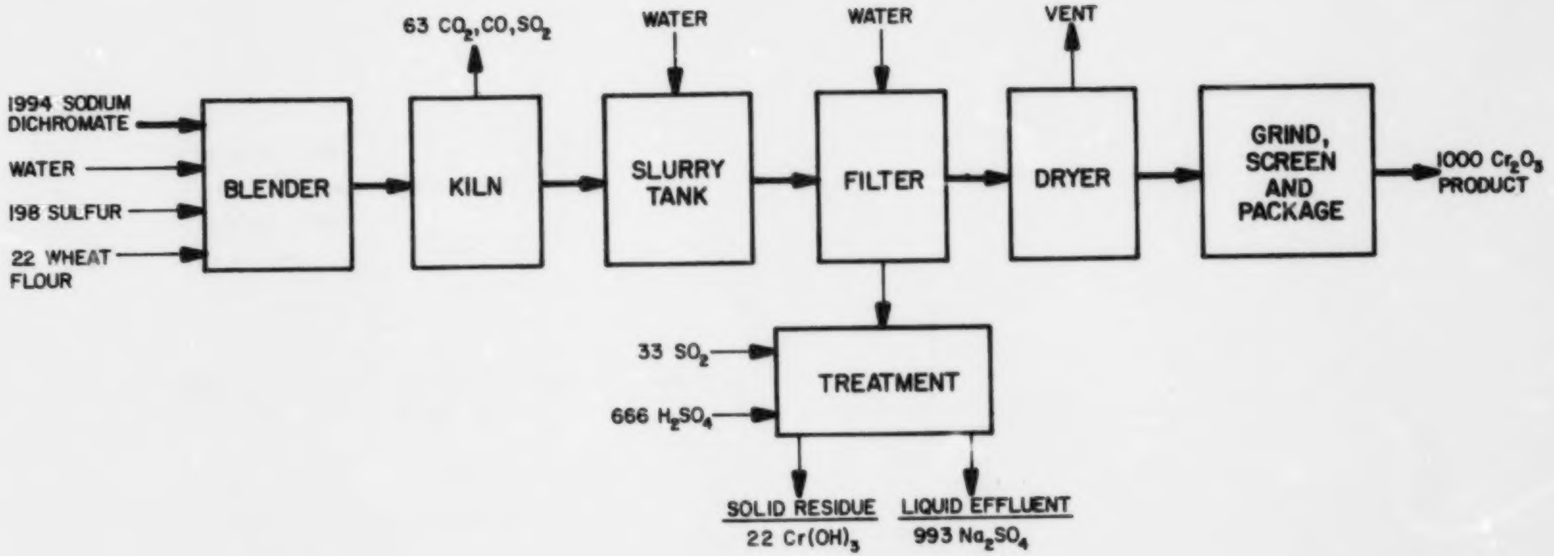


FIGURE 5-22
ANHYDROUS CHROMIC OXIDE PIGMENT MANUFACTURE

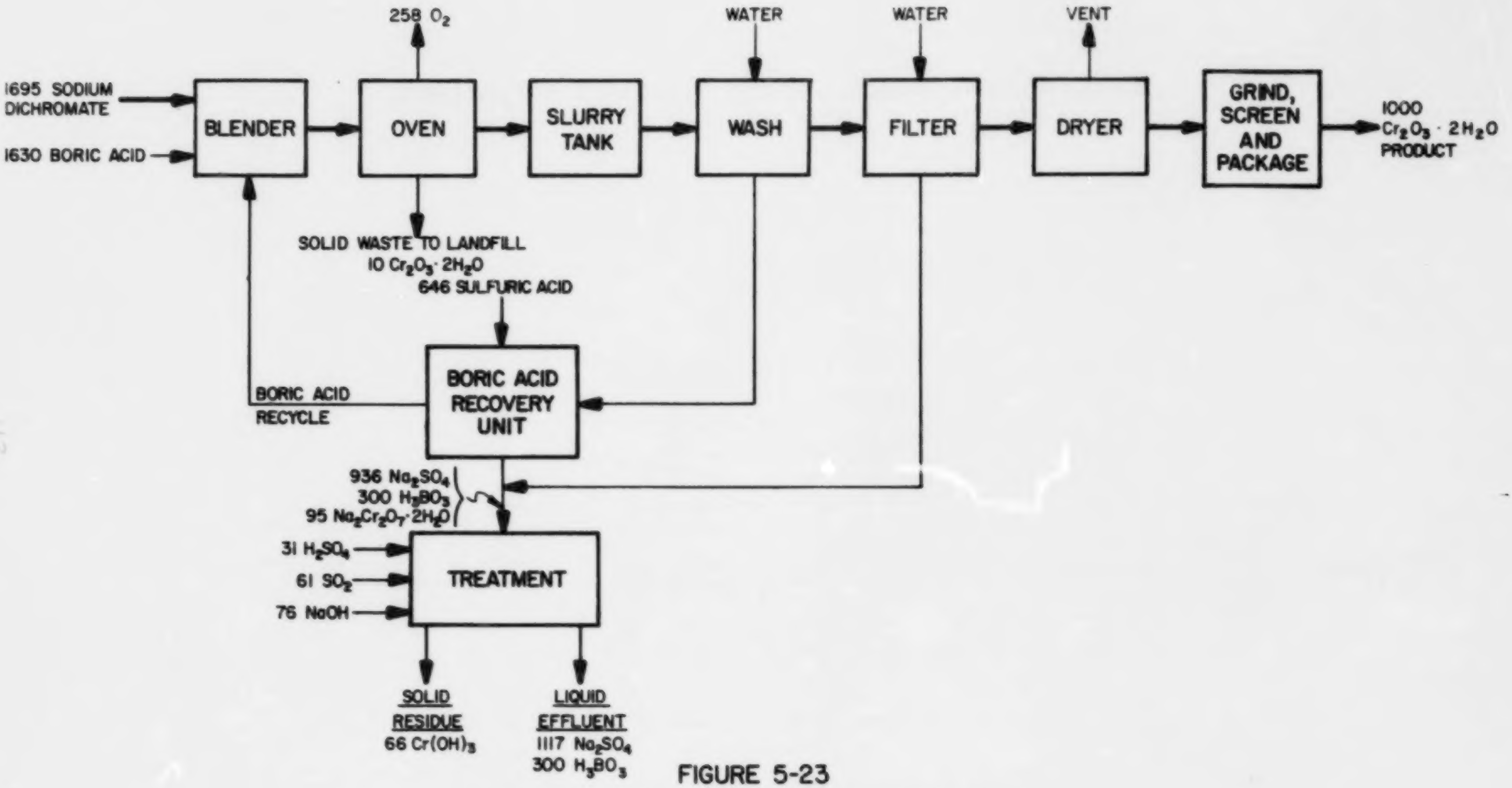


FIGURE 5-23

HYDRATED CHROMIC OXIDE MANUFACTURE

5.4.4.6 Iron Blues

Iron blues are produced by the reaction of sodium ferrocyanide, ferrous sulfate, and ammonium sulfate in solution. The product is separated by filtration, dried, and packaged as shown in Figure 5-24.

The water-borne wastes from this process contain a considerable amount of suspended product which is settled out prior to discharge. This material is then recovered as a solid waste which should have special handling due to its cyanide content. The properties of ferric ferrocyanides are discussed in Appendix A.

Chrome pigments are made in ten major locations in seven states. Average production is 17 tons per day. In five of these complexes, iron blues are also produced at an average rate of about three tons per day. These latter facilities are somewhat older, ranging in age from 20 to 60 years.

5.4.4.7 Barium Sulfate (White Extender Pigment)

Barium sulfate is produced by the reaction of barium sulfide solution with sodium sulfate as shown in Figure 5-25. It may be noted here that the product is made entirely in plants producing barium carbonate-where the sulfide is produced as an intermediate product.

In the case of barium sulfate production, the sodium sulfide is generally recovered as a salable co-product. In this case, wastes are entirely water-borne and are generally treated by aeration to oxidize soluble sulfides. There are no hazardous wastes destined for land disposal.

In one case, as shown on Figure 5-25, the soluble sulfide waste is treated by precipitating insoluble ferrous sulfide. This solid waste is considered to be non-hazardous because of its low solubility.

5.4.4.8 Cadmium Pigments

Cadmium pigments (red, orange, yellow and cadmium lithopone) are all generally produced by the method described on Figure 5-26. The amounts and types of reactants are varied to produce the desired color. Cadmium red is essentially cadmium selenide; the yellow is a mixed cadmium-zinc sulfide, and the orange is somewhere in between. Cadmium lithopone is a mixed barium sulfate-cadmium sulfide coprecipitate made by using barium sulfide to precipitate the product instead of sodium sulfide used for the other cadmium colors.

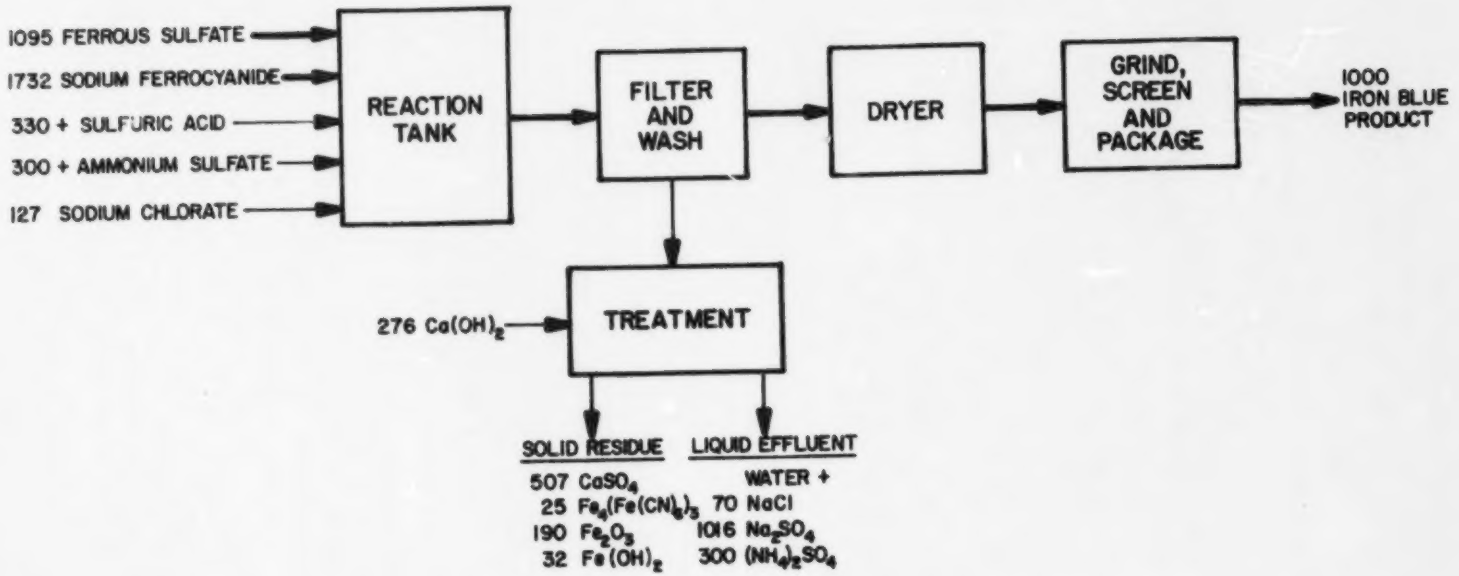


FIGURE 5-24
IRON BLUES MANUFACTURE

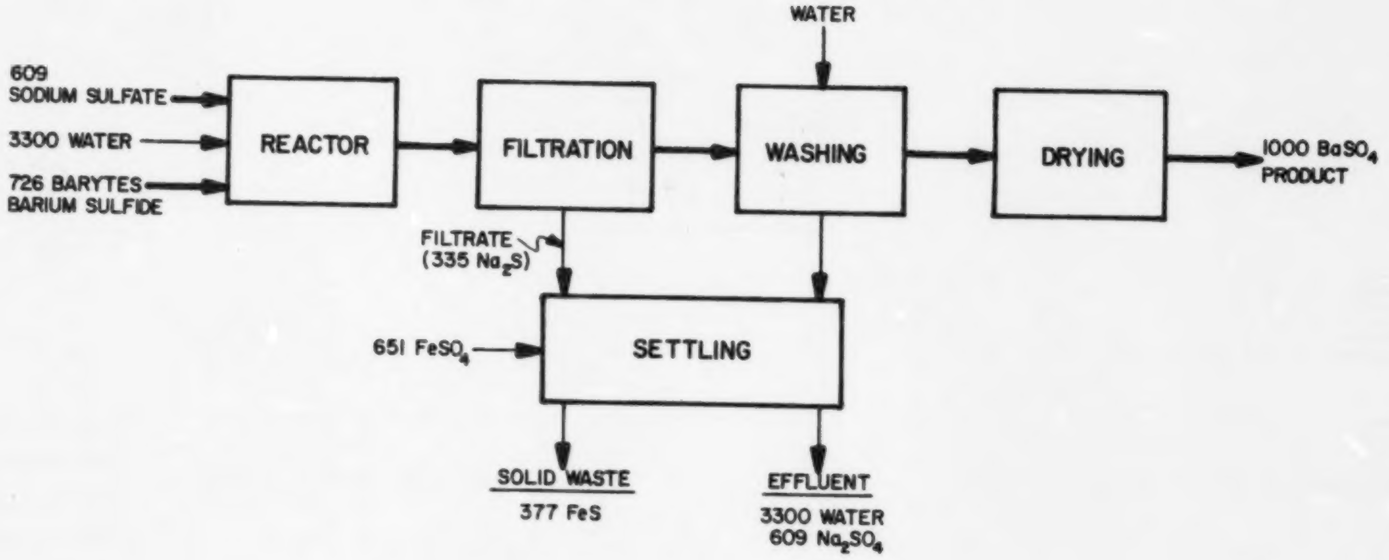


FIGURE 5-25
BARIUM SULFATE MANUFACTURE

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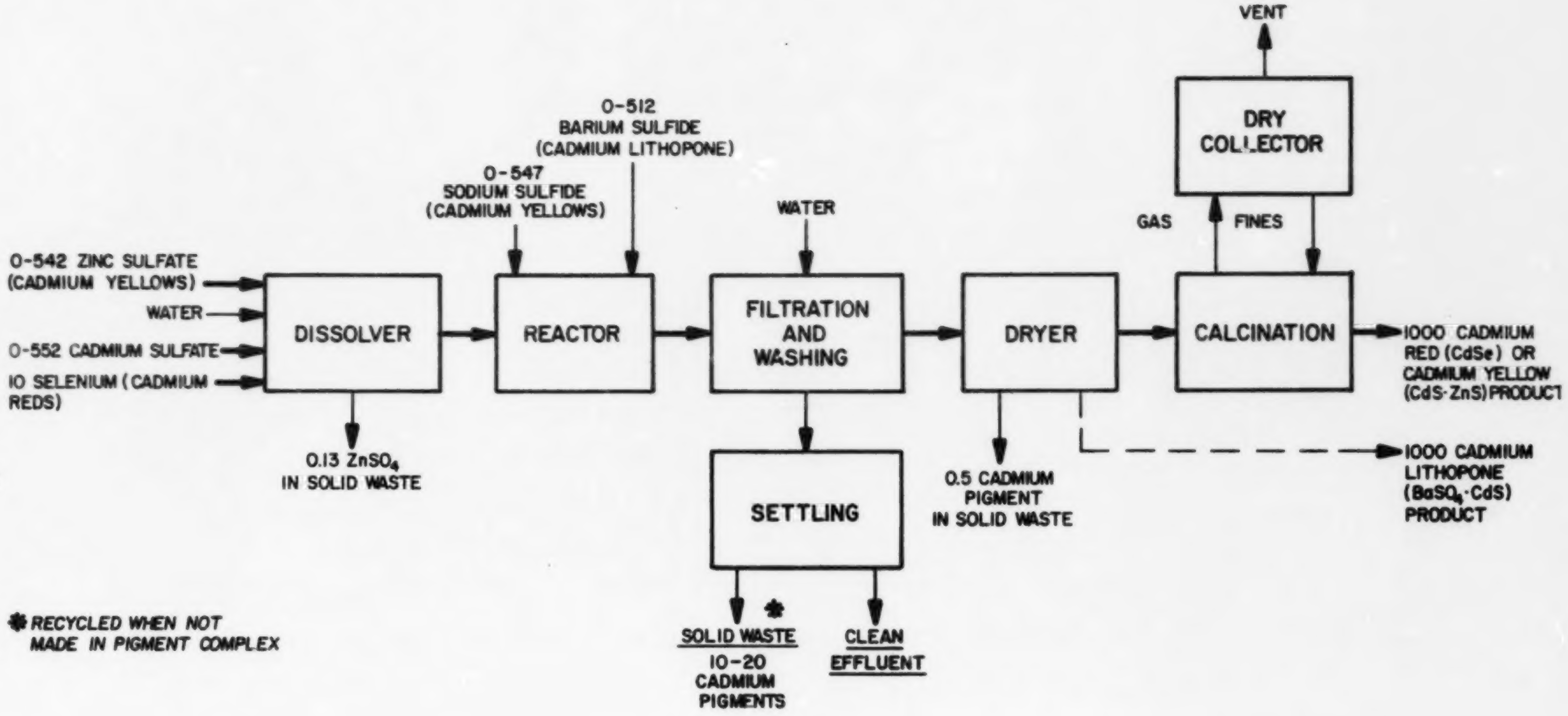

FIGURE 5-26
CADMIUM PIGMENTS MANUFACTURE

In plants producing only cadmium colors, the solid waste generated by wastewater treatment can be (and is) recycled back to the process. This cannot be done at large chrome pigment complexes where cadmium colors are made and a single large treatment facility exists for the entire complex.

The other solid waste stream destined for land disposal contains slightly contaminated dry chemical bags and in-plant product transfer containers (non-metallic).

5.4.4.9 Colored Lead Pigments (Litharge (PbO) and Red Lead (Pb_3O_4)

A mixture of powdered lead and partially oxidized powdered lead is melted and oxidized with air in a furnace to form lead monoxide directly. This is discharged by a water cooled screw conveyor to the milling operation. The product is discharged through a bag collector for storage, use, sale or further processing into a superfine grade. The only process wastes are dusts, which are collected by bag filtration and recycled. A process flow sheet is given in Figure 5-27. Red lead (Pb_3O_4) is produced by a similar process in which lead is oxidized to litharge in air, and further oxidized by heating to approximately 700°F. There are no wastes from either process.

5.4.4.10 Cobalt Pigments

Cobalt black (cobaltic oxide, Co_2O_3) is produced by the reaction shown in Figure 5-28 and is used primarily as an intermediate in the production of other cobalt compounds (These are discussed in the section on SIC 2819 chemicals.) Wastes are small and cobalt containing values are generally recycled because of the cost. Cobalt oxides have a fairly low level of toxicity, and their properties are described in Appendix A.

Cobalt blues are generally not used in ordinary paints because they are very expensive. One is a compound oxide of cobalt (30 to 35% Co_3O_4(Co_2O_3 + CoO)) and alumina (70 to 65% Al_2O_3); another is a powdered glass colored by cobalt oxide.

5.4.4.11 Iron Oxide Pigments

Iron oxide pigments are generally produced by the two methods described in Figure 5-29.

(a) Ferrous sulfate is calcined in air to the oxide which is then recovered and packaged for sale. All of the wastes arise from vent gas scrubbing and all are innocuous

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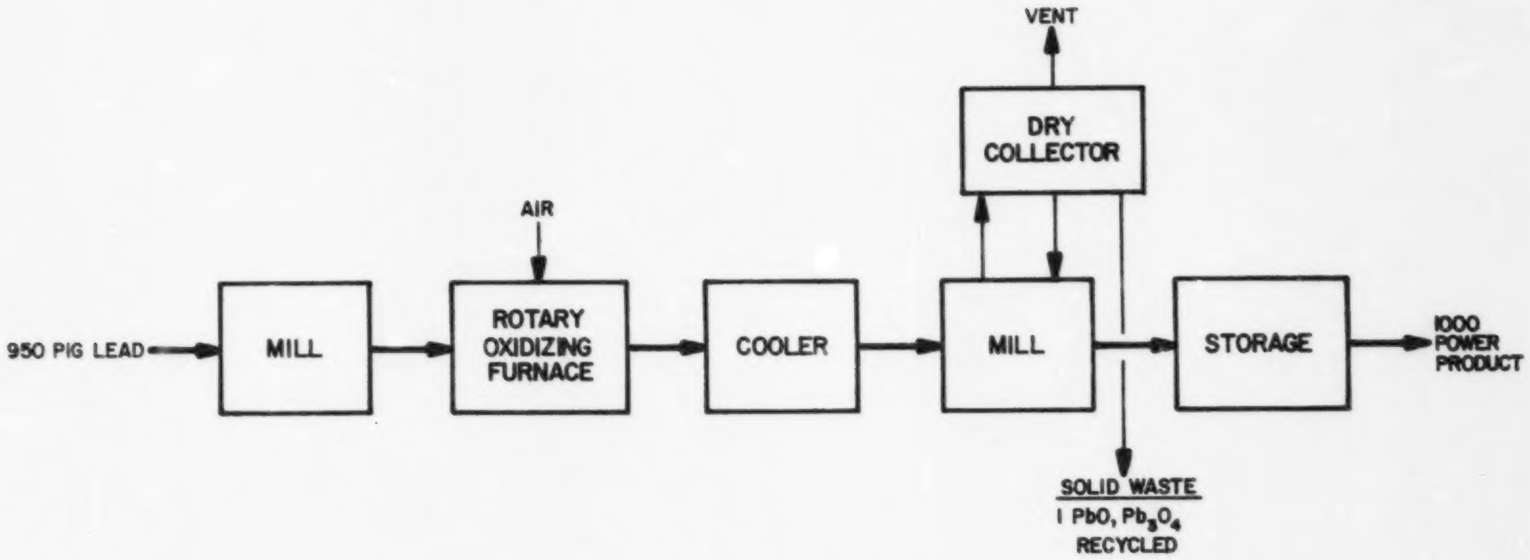


FIGURE 5-27
LEAD MONOXIDE MANUFACTURE

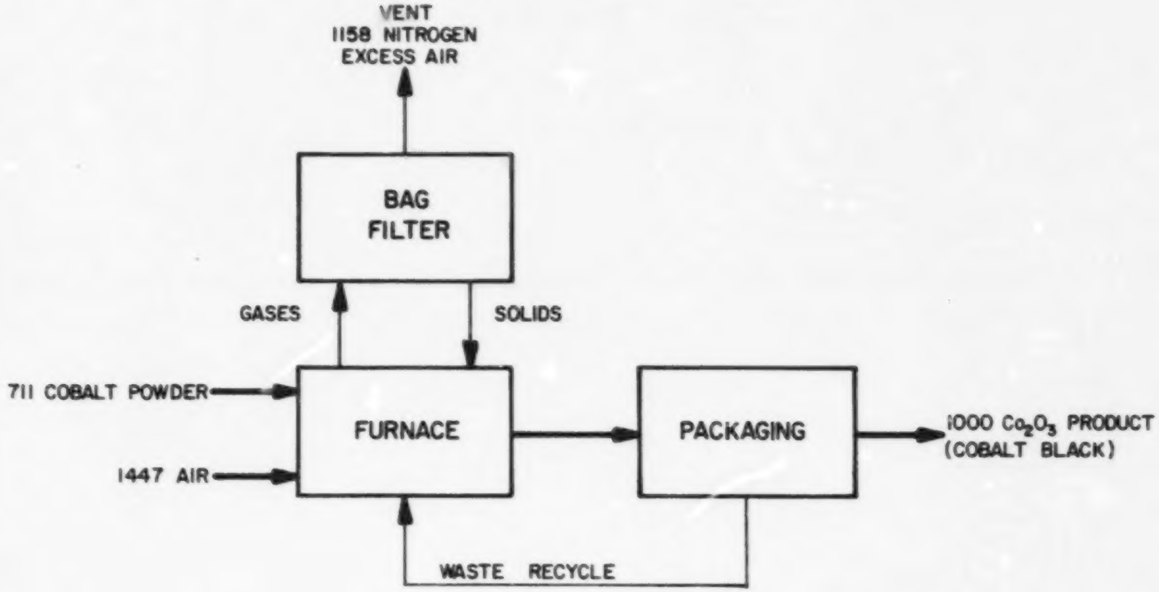


FIGURE 5-28
COBALTIC OXIDE MANUFACTURE

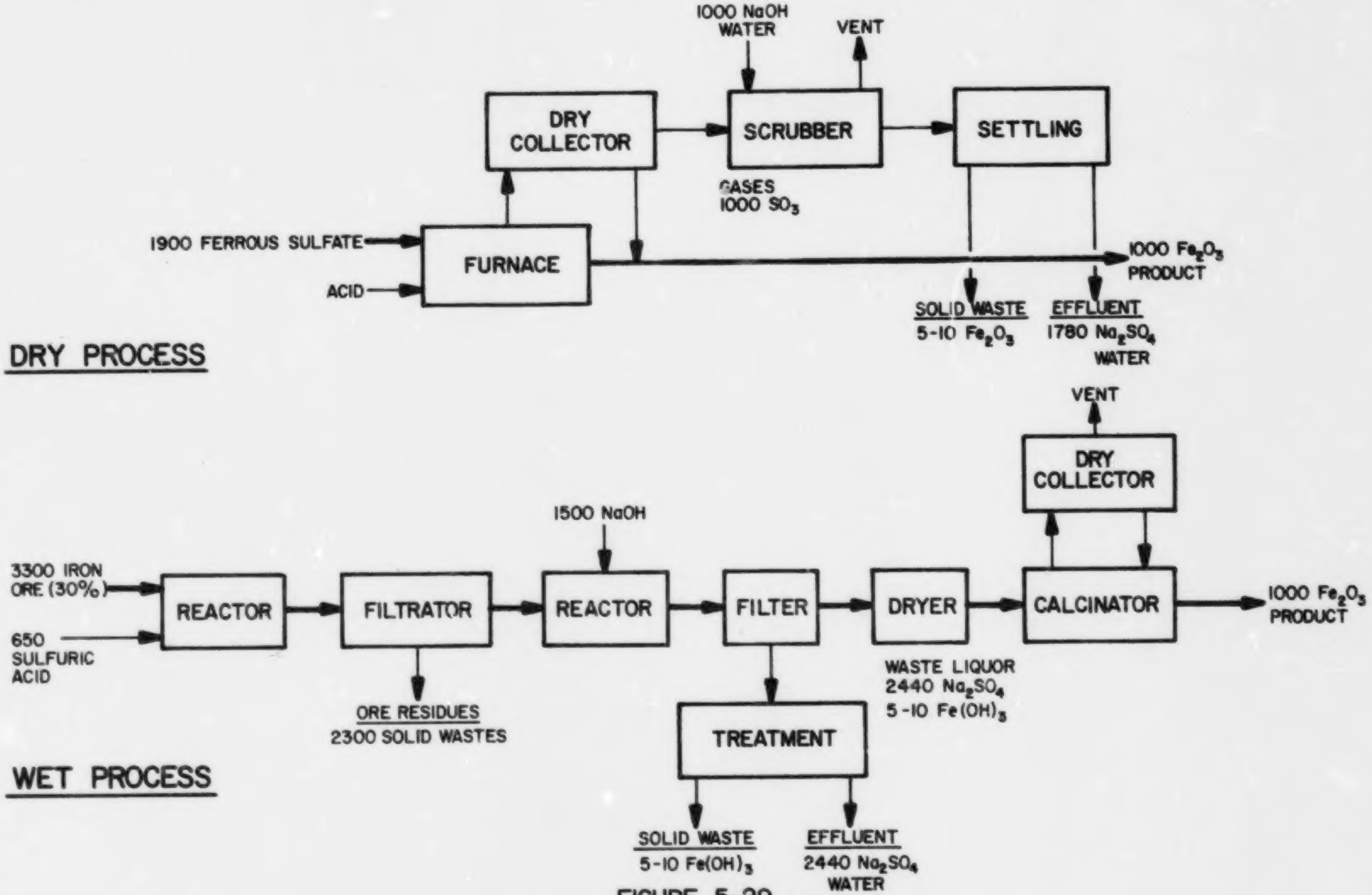


FIGURE 5-29
IRON OXIDE PIGMENTS MANUFACTURE

sulfates (i.e. Na_2SO_4 or $CaSO_4$). There are no hazardous wastes destined for land disposal.

(b) Ferrous sulfate is reacted with caustic in solution. Iron hydroxide is recovered by filtration and calcined to the oxide. Here, all wastes are also non-hazardous.

5.4.4.12 Carbon Black Pigments

Carbon black pigments are produced by the two methods shown in Figure 5-30. In the first, coal tar distillate is burned in air and the carbon formed is collected by bag filtration. In the second, acetylene is thermally decomposed to carbon and hydrogen. The carbon is recovered as the product by both processes, and there are no hazardous wastes associated with either process.

5.4.4.13 Mercuric Sulfide

This pigment is generally made by one of the two processes shown in Figure 5-31. The first involves the reaction of hydrogen sulfide gas with a solution of mercuric chloride to precipitate the product, black mercuric sulfide. This process requires wastewater treatment which generates about 1.5 kilograms of mercuric oxide solid waste per metric ton of product.

The other process is a direct reaction of mercury metal with sulfur to form the black mercuric oxide product. No water in involved. Further sublimation steps on the black product produces red mercuric sulfide. This process does not generate land-destined hazardous wastes.

5.4.4.14 Ultramarine Pigment

Ultramarine is a blue, complex sodium aluminum silicate and sulfide, made by heating together sodium carbonate, kaolin, charcoal, quartz, sulfur, sodium sulfate, and resin. It is absolutely essential that iron not be present in all raw materials, as it appreciably dulls the color. The melt is cooled, ground, washed free of water soluble salts, and heated with more sulfur until a blue color develops. A darker blue may be produced by substituting sodium sulfate for sodium carbonate.

The manufacture of this product is illustrated in Figure 5-32. Only waterborne wastes of sodium salts are generated in the production of ultramarine pigment. No wastes are disposed of on land, nor are any hazardous wastes generated by treatment of air or water wastes.

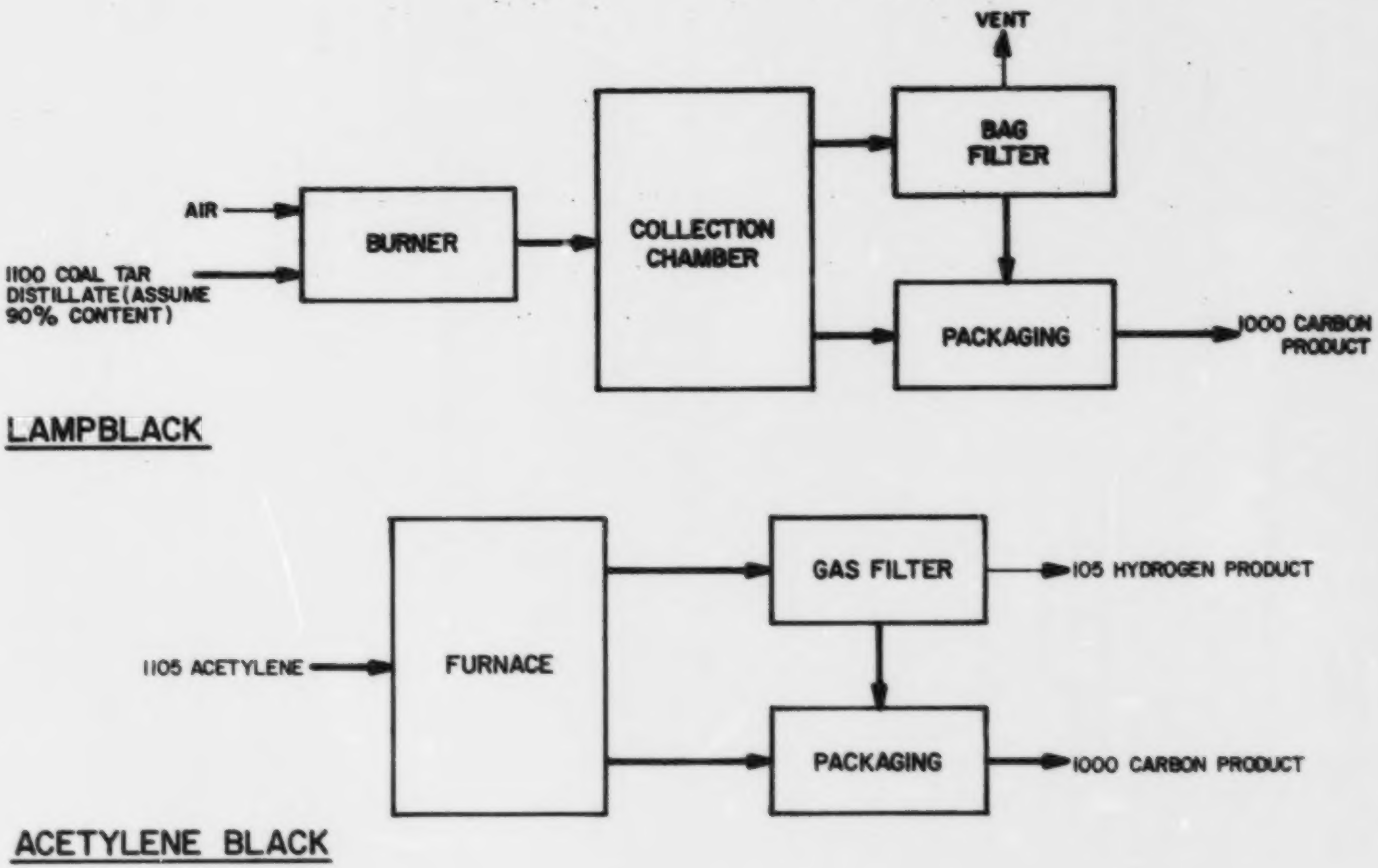


FIGURE 5-30
CARBON BLACK MANUFACTURE

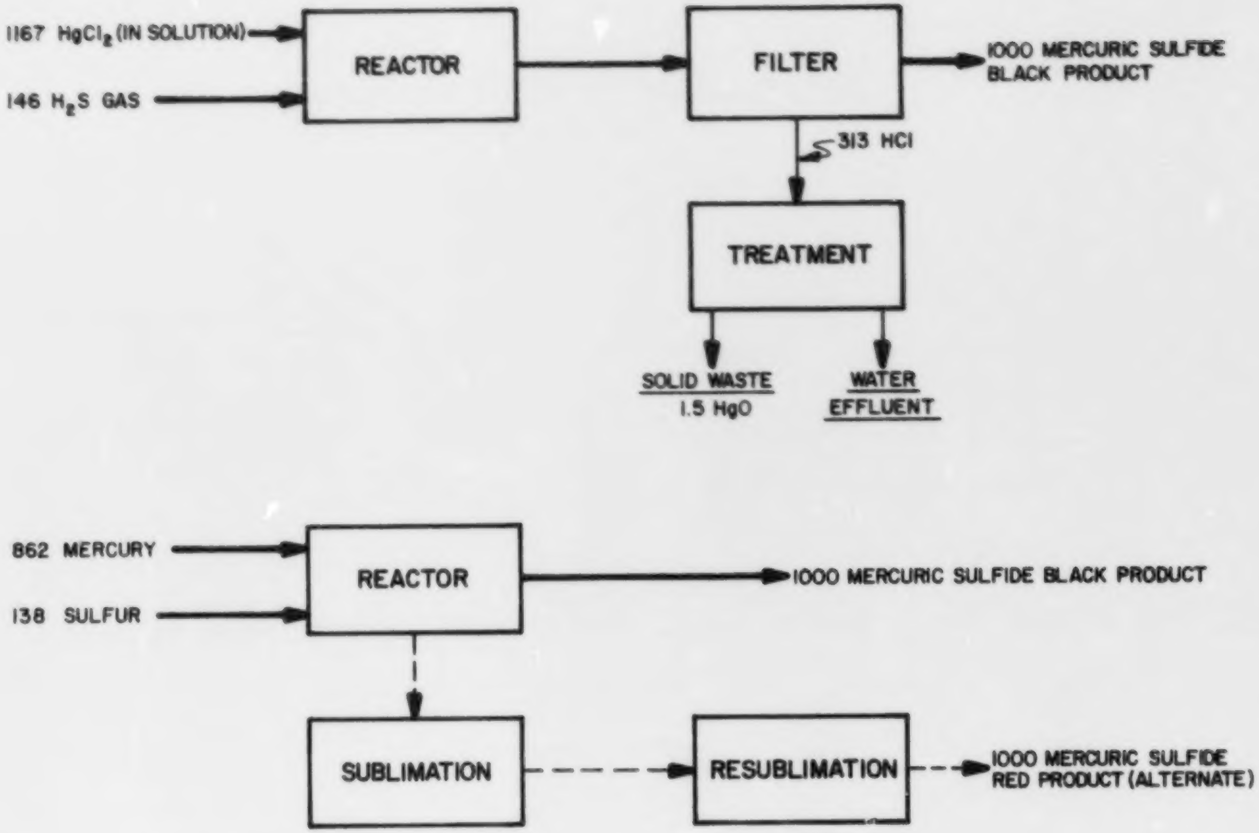
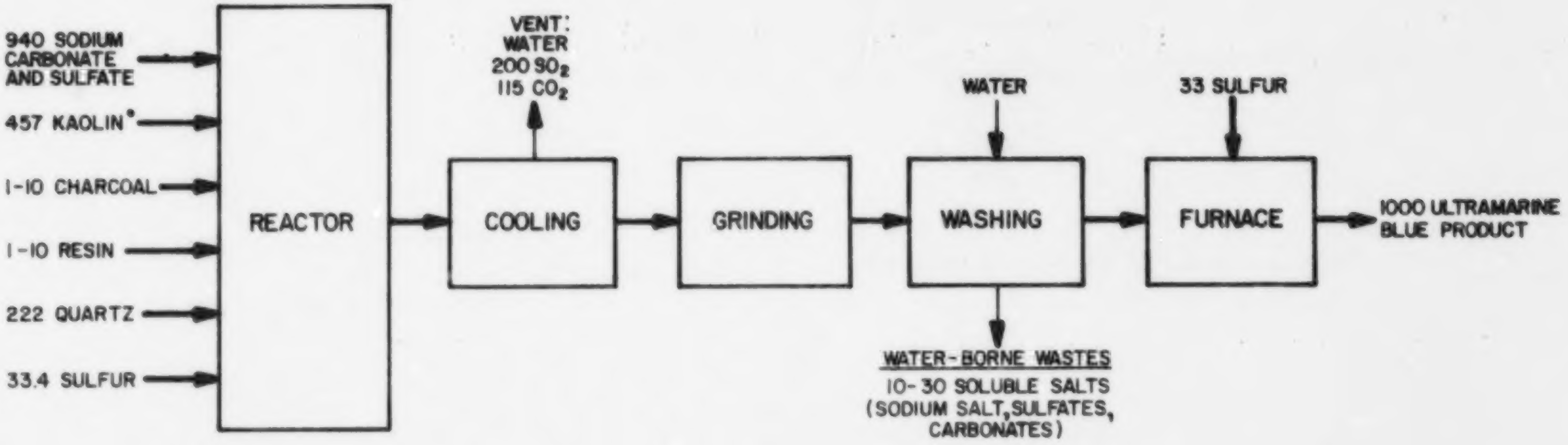


FIGURE 5-31
MERCURIC SULFIDE MANUFACTURE



* KAOLIN: 245 SiO_2, 212 Al_2O_3 (DRY BASIS)

FIGURE 5-32
ULTRAMARINE BLUE MANUFACTURE

5.4.4.15 Aggregate of SIC 28163 Hazardous Wastes to Land Disposal

The amounts of the constituents of the several waste streams containing hazardous materials in sufficient quantities to be hazardous in total are shown for the typical operation in the flow diagrams in the preceding sections. The values given are relative to the product rate, that is, they are numerically equivalent to either kilograms per metric ton of product or pounds per 1000 pounds of product. The hazardous waste streams from this industrial subcategory come primarily from the manufacture of chrome pigments and iron blues, with lesser amounts accumulative from the manufacture of cadmium and mercury colors. The hazardous constituents in these waste streams are chromium compounds, lead compounds, cyanide compounds, zinc compounds, cadmium compounds, and mercury compounds. Practically all of these waste streams are the result of wastewater treatment to remove the undesirable constituents from the plants' effluent. The water content of these waste streams can range from 30-60 percent depending on whether they are filter cakes or sludges.

Table 5-6 lists the aggregate hazardous waste streams of SIC 28163 on a state-by-state, regional and total U. S. basis and the amounts of the various hazardous constituent materials which is estimated to be currently valid. The local situations in each state when they deviate from the "typical" are taken into account insofar as is possible. The data of this table are comprised of the most reliable and more consistent entries from several sources:

(a) calculated from manufacturers' data that has been found to be consistent and hence reliable
(b) estimated from fragmentary or equivocal manufacturer's data
(c) estimated from waste disposal contractors's data, and
(d) our own estimates.

The hazardous constituents in all cases are given in terms of the compounds shown on the flow diagrams.

The largest amount of hazardous constituents arise from the chrome pigments and iron blues sector of the industry. This amounts to about 4300 metric tons per year on a dry basis which is about 54 percent of the total dry basis waste stream (approximately 8000 metric tons per year). The other colored pigments part of the industry contributes only 54 metric tons per year of hazardous constituents or less than 1 percent of the total for the industry. Over 90 percent (on a dry basis) of the total hazardous waste streams

Table 5-6. Hazardous Wastes Destined for Land Disposal Currently Generated by Industry Subcategory 28163, Chrome Colors and Other Pigments (metric tons per year, dry basis)

		Chrome Pigments & Iron Blues					Other Colored Pigments				Total 28163 Hazardous Wastes
		Total Hazardous Wastes	Chromium Compounds	Lead Compounds	Zinc Compounds	Cyanide Compounds	Total Hazardous Wastes	Cadmium Compounds	Mercury Compounds	Zinc Compounds	
IV	Alabama										
X	Alaska										
IX	Arizona										
VI	Arkansas										
IX	California										
VIII	Colorado										
I	Connecticut										
III	Delaware										
IV	Florida										
IV	Georgia										
IX	Hawaii										
X	Idaho										
V	Illinois										
V	Indiana										
VII	Iowa										
VII	Kansas										
IV	Kentucky	210	120	98							210
VI	Louisiana										
I	Maine										
III	Maryland	740	480	200	150		24*	18		0.15	740
I	Massachusetts										
V	Michigan										
V	Minnesota										
IV	Mississippi										
VII	Missouri										
VIII	Montana										
VII	Nebraska										
IX	Nevada										
I	New Hampshire										
II	New Jersey	1,800	870	530	130	10	0.31	0.22		0.06	1,800
VI	New Mexico										
II	New York	3,400	760	460	12	75	3,024*	36	0.3	0.3	3,400
IV	North Carolina										
VIII	North Dakota										
V	Ohio	260	20	16		7.5					260
VI	Oklahoma										
X	Oregon										
III	Pennsylvania	110	110								110
I	Rhode Island										
IV	South Carolina										
VIII	South Dakota										
IV	Tennessee										
VI	Texas										
VIII	Utah										
I	Vermont										
III	Virginia										
X	Washington										
III	West Virginia	1,500	180	140		44					1,500
V	Wisconsin										
VIII	Wyoming										
TOTAL		8,000	2,500	1,400	290	140	3,000*	54	0.3	0.5	8,000
Region I											
II		5,200	1,630	990	142	85	3,024*	36	0.3	0.36	5,200
III		2,000	770	340	150	44	24*	18		0.16	2,000
IV		210	120	98							210
V		260	20	16		7.5					260
VI											
VII											
VIII											
IX											
X											

*Does not reflect the actual numerical total since it includes compounds from the other category (i.e., Chrome Pigments and Iron Blues).

destined for land disposal are currently generated in EPA Regions II and III.

5.4.4.16 Projection of SIC 28163 Hazardous Wastes to 1977 and 1983

The chrome colors and related pigments industry is a stable and well-developed industry that is expected to grow at about the same rate as the whole economy. The impact of air and water regulations will to bring more of the hazardous wastes generated by these processes to land disposal. Recycle or reuse of wastes is now practiced wherever possible. Purity and quality of product is paramount in this industry, so recycling of contaminated materials is generally not possible.

The individual growth factors used in the forward projection of the SIC 28163 hazardous wastes include:

(a) an assumed 3 percent per year normal growth of the industry, and
(b) the additional solid wastes generated by recommended 1977 and 1983 treatment technology to improve effluent water quality which is expected to be significant in the chrome pigments industry.

Tables 5-7 and 5-8 give the projected amounts of wastes in the same format as was presented in Table 5-6. State-by-state, regional and total U. S. aggregates are given for the various waste streams for the total hazardous waste to land disposal.

The total amounts of hazardous waste streams (on a dry basis) in metric tons per year projected for SIC 28163 are summarized as follows:

Period	Current	1977	1983
Total Hazardous Constituents	4300	5200	6100
Total Hazardous Waste Stream	8000	9100	11,000

5.4.5 Summary of Waste Streams Destined for Land Disposal From SIC 2816

The total amounts of hazardous waste destined for land disposal from the three five-digit SIC industry subcategories are summarized as follows (metric tons per year, dry basis):

Table 5-7. Hazardous Wastes Destined for Land Disposal Expected to be Generated in 1977 by Industry Subcategory 28163, Chrome Colors and Other Pigments, (metric tons per year, dry basis)

		Chrome Pigments & Iron Blues					Other Colored Pigments				Total 28163 Hazardous Wastes
		Total Hazardous Wastes	Chromium Compounds	Lead Compounds	Zinc Compounds	Cyanide Compounds	Total Hazardous Wastes	Cadmium Compounds	Mercury Compounds	Zinc Compounds	
IV	Alabama										
X	Alaska										
IX	Arizona										
VI	Arkansas										
IX	California										
VIII	Colorado										
I	Connecticut										
III	Delaware										
IV	Florida										
IV	Georgia										
IX	Hawaii										
X	Idaho										
V	Illinois										
V	Indiana										
VII	Iowa										
VII	Kansas										
IV	Kentucky	240	140	110							240
VI	Louisiana										
I	Maine										
III	Maryland	870	560	230	170		27*	20		0.17	870
I	Massachusetts										
V	Michigan										
V	Minnesota										
IV	Mississippi										
VII	Missouri										
VIII	Montana										
VII	Nebraska										
IX	Nevada										
I	New Hampshire										
II	New Jersey	1,700	1,000	610	150	11	0.33*	0.25		0.07	2,000
VI	New Mexico										
II	New York	3,800	890	530	14	84	3,800*	40	0.34	0.35	3,800
IV	North Carolina										
VIII	North Dakota										
V	Ohio	300	24	18		8					300
VI	Oklahoma										
X	Oregon										
III	Pennsylvania	130	130								130
I	Rhode Island										
IV	South Carolina										
VIII	South Dakota										
IV	Tennessee										
VI	Texas										
VIII	Utah										
I	Vermont										
III	Virginia										
X	Washington										
III	West Virginia	1,700	230	160		50					1,700
V	Wisconsin										
VIII	Wyoming										
TOTAL		8,700	3,000	1,700	330	150	3,800*	60	0.34	0.6	9,100
Region I											
II		5,500	1,900	1,100	160	95	3,800*	40	0.34	0.4	5,800
III		2,700	920	390	170	50	27*	20		0.2	2,700
IV		240	140	110							240
V		300	24	18		8					300
VI											
VII											
VIII											
IX											
X											

*Does not reflect the actual numerical total since it includes compounds from the other category (i.e., Chrome Pigments and Iron Blues).

Table 5-8. Hazardous Wastes Destined for Land Disposal Expected to be Generated in 1983 by Industry Subcategory 28163, Chrome Colors and Other Pigments, (metric tons per year, dry basis)

		Chrome Pigments & Iron Blues					Other Colored Pigments				Total 28163 Hazardous Wastes
		Total Hazardous Wastes	Chromium Compounds	Lead Compounds	Zinc Compounds	Cyanide Compounds	Total Hazardous Wastes	Cadmium Compounds	Mercury Compounds	Zinc Compounds	
IV	Alabama										
X	Alaska										
IX	Arizona										
VI	Arkansas										
IX	California										
VIII	Colorado										
I	Connecticut										
III	Delaware										
IV	Florida										
IV	Georgia										
IX	Hawaii										
X	Idaho										
V	Illinois										
V	Indiana										
VII	Iowa										
VII	Kansas										
IV	Kentucky	290	170	130							290
VI	Louisiana										
I	Maine										
III	Maryland	1,000	660	260	200		32*	24		0.2	1,000
I	Massachusetts										
V	Michigan										
V	Minnesota										
IV	Mississippi										
VII	Missouri										
VIII	Montana										
VII	Nebraska										
IX	Nevada										
I	New Hampshire										
II	New Jersey	2,400	1,220	720	170	13	0.42*	0.3		0.08	2,400
VI	New Mexico										
II	New York	4,500	1,070	630	16	100	4,050*	48	0.4	0.4	4,500
IV	North Carolina										
VIII	North Dakota										
V	Ohio	360	28	21		10					360
VI	Oklahoma										
X	Oregon										
III	Pennsylvania	150	150								150
I	Rhode Island										
IV	South Carolina										
VIII	South Dakota										
IV	Tennessee										
VI	Texas										
VIII	Utah										
I	Vermont										
III	Virginia										
X	Washington										
III	West Virginia	2,000	250	190		59					2,000
V	Wisconsin										
VIII	Wyoming										
TOTAL		11,000	2,500	2,000	390	180	4,100*	72	0.4	0.7	11,000
Region I											
II		6,900	2,300	1,300	190	110	4,050*	48	0.4	0.5	6,900
III		3,100	1,100	470	200	59	32*	24		0.2	3,100
IV		290	170	130							290
V		360	28	21		10					360
VI											
VII											
VIII											
IX											
X											

*Does not reflect the actual numerical total since it includes compounds from the other category (i.e., Chrome Pigments and Iron Blues).

Period	Current	1977	1983
SIC 28161 Haz. Const.	350	560	800
Total Stream	151,000	222,000	310,000
SIC 28162 Haz. Const.	12	14	16
Total Stream	240	270	320
SIC 28163 Haz. Const.	4300	5200	6100
Total Stream	8000	9100	11,000

It is obvious that SIC 28163 (Chrome Colors and Other Inorganic Pigments) generates the most hazardous constituents while SIC 28161 (Titanium Dioxide Pigments) generates the largest amount of total waste stream containing hazardous constituents.

5.5 Other Industrial Inorganic Chemicals (SIC 2819)

This category of the industrial inorganic chemicals manufacturing industries covers a large number of miscellaneous inorganic chemicals broken down into the following subcategories:

sulfuric acid (SIC 28193)
other inorganic acids (SIC 28194)
aluminum oxide (SIC 28195)
other aluminum compounds (SIC 28196)
potassium and sodium compounds (SIC 28197)
chemical catalytic preparations (SIC 28198)
other inorganic chemicals, not elsewhere classified (SIC 28199)

In this section, the discussion is limited to those SIC 2819 chemicals having a volume of manufacture that is of significant economic importance and wastes sufficient to merit consideration. Product value below one million dollars annually was considered insignificant for this purpose. Commodities in this volume category were judged not to produce significant quantities of waste since their manufacturing volume is so low. This does not preclude a single manufacturer at a single location in one of these low volume commodities from having a hazardous waste problem. However none of this sort were found.

5.5.1 Sulfuric Acid (SIC 28193)

In the contact process, which is the principal process for manufacturing sulfuric acid, purified and dry sulfur dioxide is mixed with air, heated, and introduced into a reactor containing a platinum or vanadium pentoxide catalyst. The resulting gas mixture is cooled and sent to a series of internally-cooled towers where the sulfur trioxide is absorbed by oleum (acid plus excess sulfur trioxide) of successively decreasing sulfur trioxide concentrations. Acid less than 97 percent concentration cannot be used to absorb sulfur trioxide because of mist formation and resulting sulfur trioxide losses. Various products ranging in acidic strength from battery acid (33.5 percent H_2SO_4) to 70 percent oleum (70 percent free SO_3 in H_2SO_4) are produced. The only wastes are those generated by alkaline scrubbing of tail gases and neutralization of product leaks and spills. The wastes generated by these operations are either waterborne or solid (gypsum), and are not hazardous. The following diagram for the principal process (Contact Process) is given in Figure 5-33, and that of the outmoded (but still used) Chamber Process in Figure 5-34. SIC 281 production of sulfuric acid results from burning of sulfur in the above processes. By-product sulfuric acid from other industries is also produced. Spent acid from the oil refining industry is burned with fuel in a modified contact process to reclaim the acid. The non-ferrous metal industry produces by-product sulfuric acid from the sulfur dioxide recovered in ore roasting processes.

5.5.2 Other Inorganic Acids (SIC 28194)

5.5.2.1 Hydrochloric Acid

Hydrochloric acid is produced either as a by-product of organic chlorinations or by direct synthesis, in the reaction of chlorine with hydrogen. The former process is not in SIC 281. In the latter process, hydrogen and chlorine gases are reacted in a vertical burner. The product hydrogen chloride is cooled and then absorbed in water. Exhaust gases are scrubbed and acid values are recycled. End products may include strong acid (22°Be) from the cooler, weak acid (18 °Be) from the absorber column, a mixture of these (20°Be), or anhydrous HCl. The anhydrous acid may be prepared by stripping gaseous HCl from strong acid. The condensate and column bottoms may then be recycled to the process. All wastes originate from wet scrubbing of tail gases to remove acidic gases and are waterborne. They consist of alkali metal or alkali earth chlorides. No hazardous wastes are generated by these processes. The major process is given in Figure 5-35, and two minor (and outmoded) processes that are still practiced in a few locations are given in Figures 5-36 and 5-37. Note that the concentrations of commercially standard hydrochloric acid solutions are given in the flow diagrams in terms of degrees Baume (°Be). These are measurements of density on a hydrometer scale and are standard terminology in this industry.

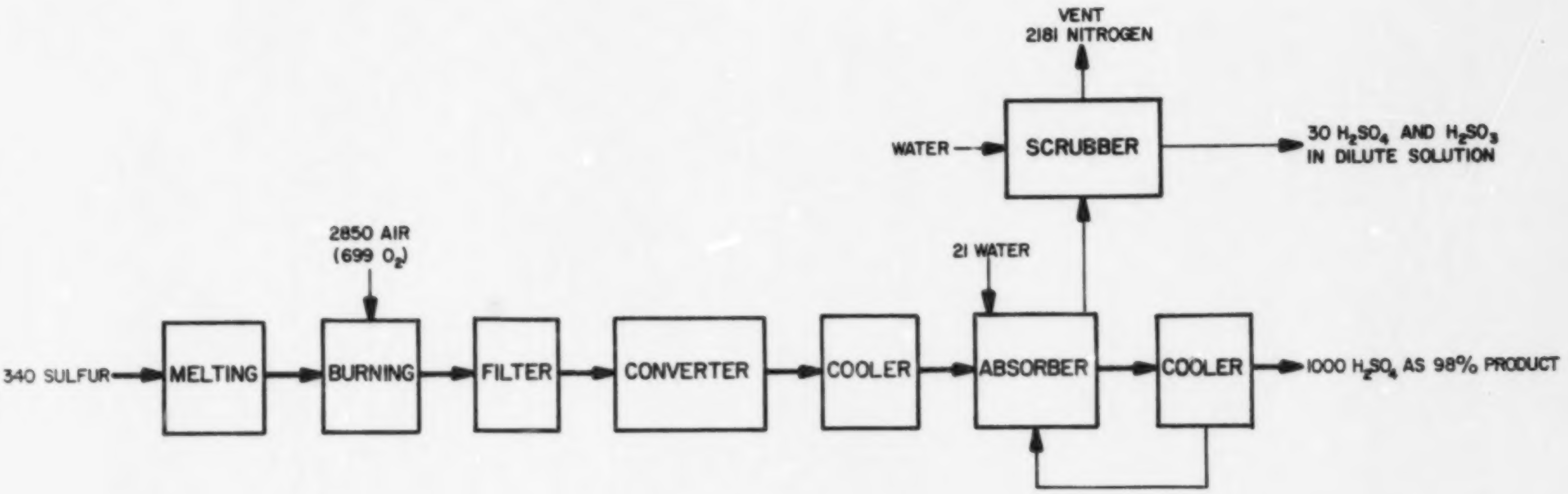


FIGURE 5-33
SULFURIC ACID MANUFACTURE
BY THE CONTACT PROCESS

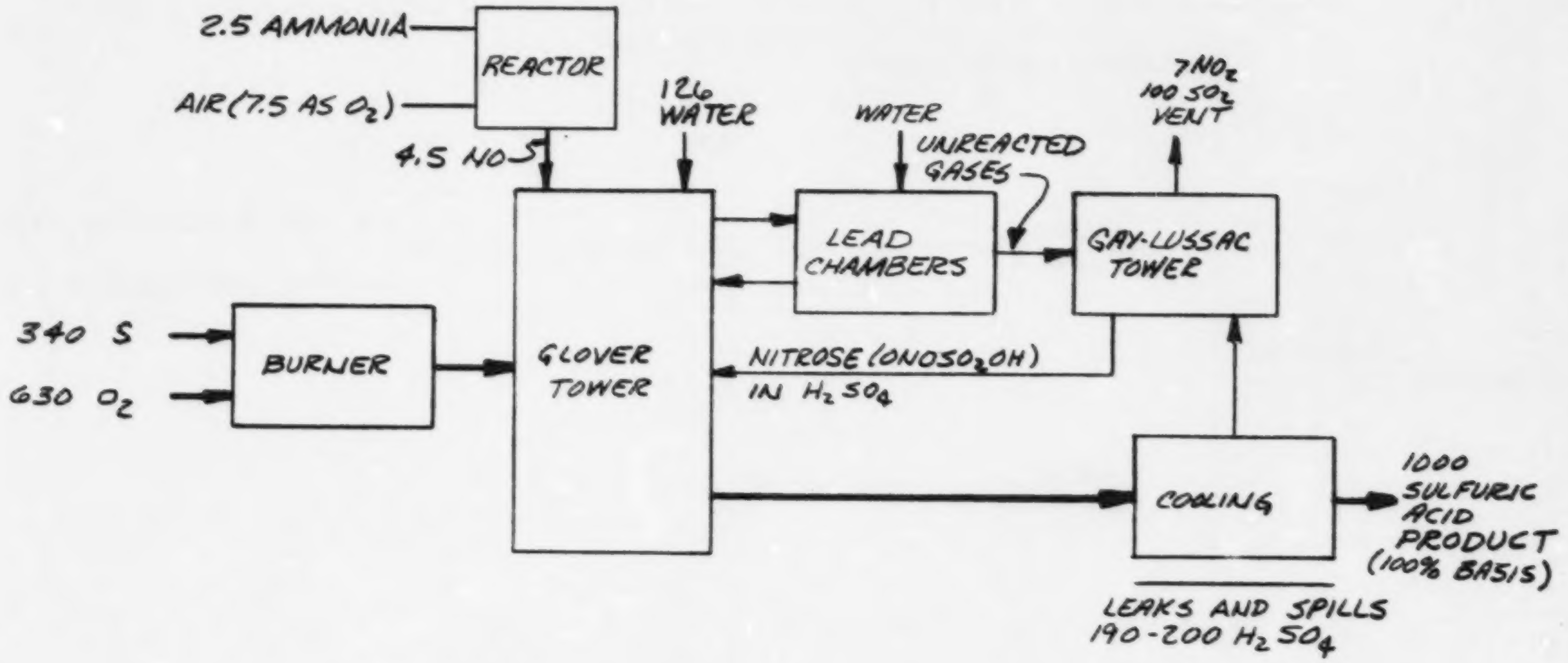


FIGURE 5-34
SULFURIC ACID MANUFACTURE
BY THE CHAMBER PROCESS

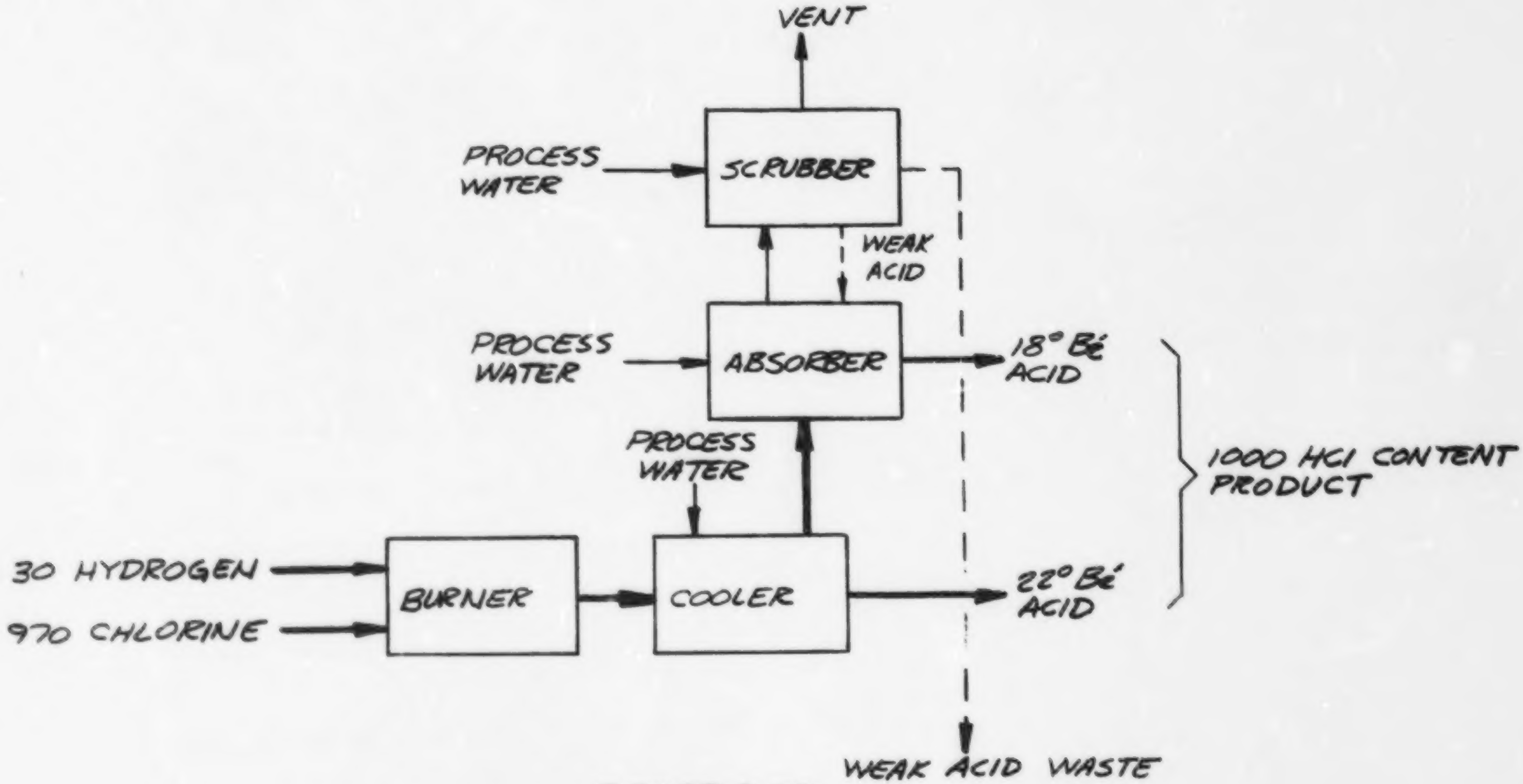


FIGURE 5-35
HYDROCHLORIC ACID MANUFACTURE

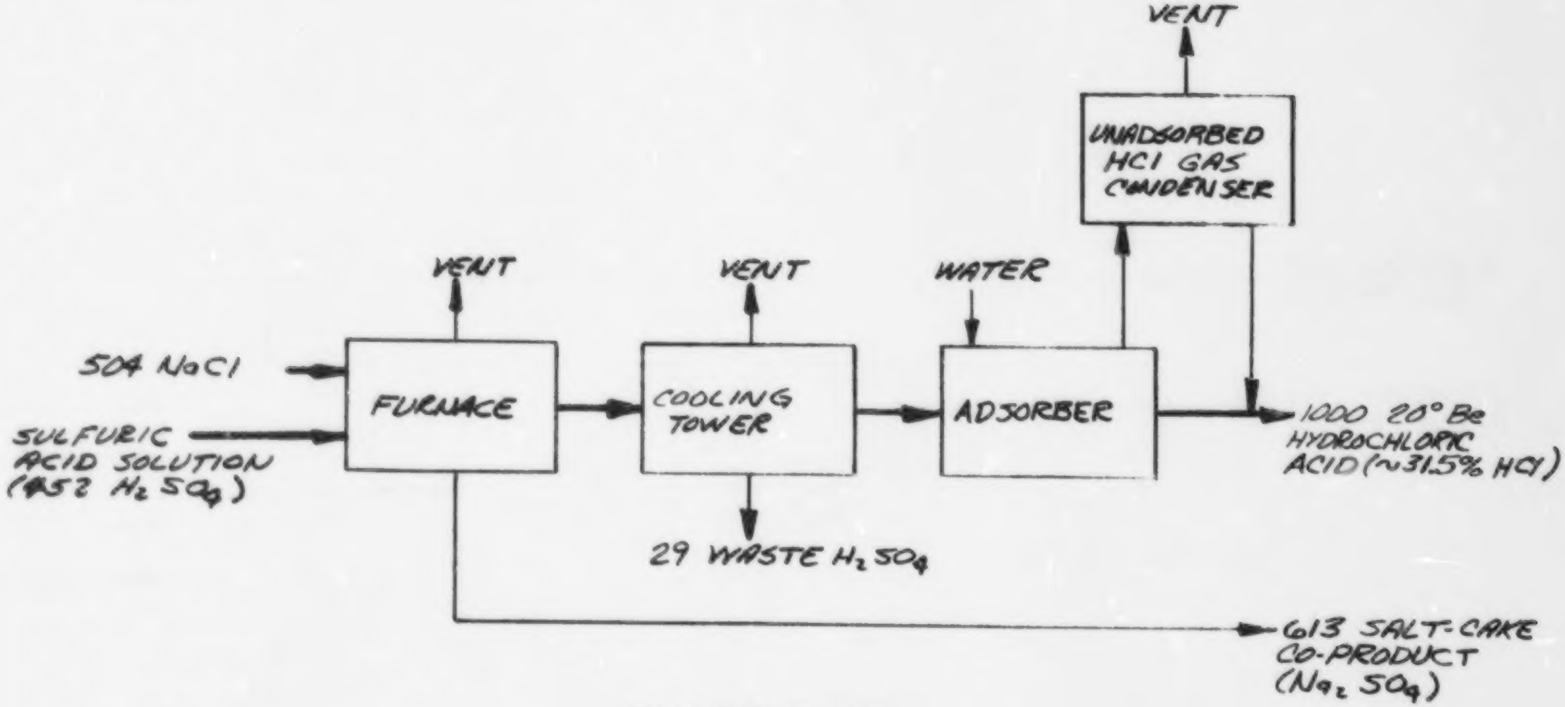

VENT
UNADSORBED HCl GAS CONDENSER
VENT
VENT
WATER
504 NaCl
SULFURIC ACID SOLUTION (85% H2SO4)
FURNACE
COOLING TOWER
ADSORBER
1000 20° Be HYDROCHLORIC ACID (~31.5% HCl)
29 WASTE H2SO4
613 SALT-CAKE CO-PRODUCT (Na2SO4)

FIGURE 5-36

HYDROCHLORIC ACID MANUFACTURE BY THE SALT-SULFURIC ACID PROCESS

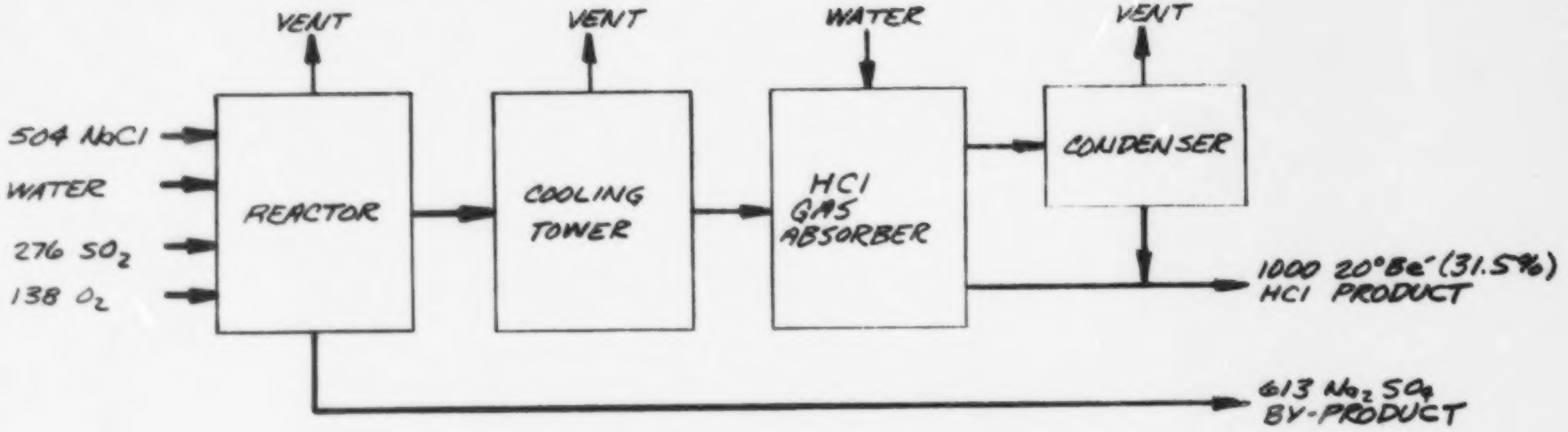


FIGURE 5-37

HYDROCHLORIC ACID MANUFACTURE
BY THE HARGREAVES PROCESS

5.5.2.2 Boric Acid

This product is made by acidulation of borax. From the acidulator, the boric acid solution is fed to a vacuum crystallizer, where boric acid crystals are formed, and then to a filter. The sodium sulfate is removed in the filtrate, and the technical grade boric acid is dried and packaged. The technical grade product can also be diverted upstream of the final drying step, redissolved, crystallized, filtered, and dried to produce a higher purity product. Sodium sulfate is a co-product and most of the wastes are waterborne. There are small amounts of arsenic-bearing wastes which are potentially hazardous upon land disposal, but at present they are all discharged in the plant effluent. The properties of arsenic are described in Appendix A. This waste occurs at only one plant. The impact of effluent discharge limitations should cause arsenic wastes to go to land disposal in 1977. The flow diagram for this process is given in Figure 5-38.

5.5.2.3 Chromic Acid

This chemical is discussed in SIC Code 28199 under chromate production. There are no wastes that are not attributable to the manufacture of sodium dichromate. The flow diagram for chromic acid manufacture is given in Figure 5-39.

5.5.2.4 Hydrogen Cyanide

Hydrogen cyanide is produced from methane, ammonia, and air by a catalytic process (Andrussow Process) whose flow diagram is shown in Figure 5-40. This reaction occurs at elevation temperatures over a platinum catalyst. Other products and product contaminants include residual ammonia and organic nitrites. Unreacted ammonia is removed from the products by scrubbing with sulfuric acid. The crude cyanide is then further purified by scrubbing with water and distillation of the aqueous solution. The purified product is compressed and liquified. All of the hazardous wastes (cyanides) are waterborne and are generally removed by either chemical oxidation or biological treatments. No hazardous wastes destined for land disposal are generated by the treatments.

Small amounts of HCN are also generated as a co-product of acrylonitrile manufacture, and there are no hazardous wastes attributable to this process.

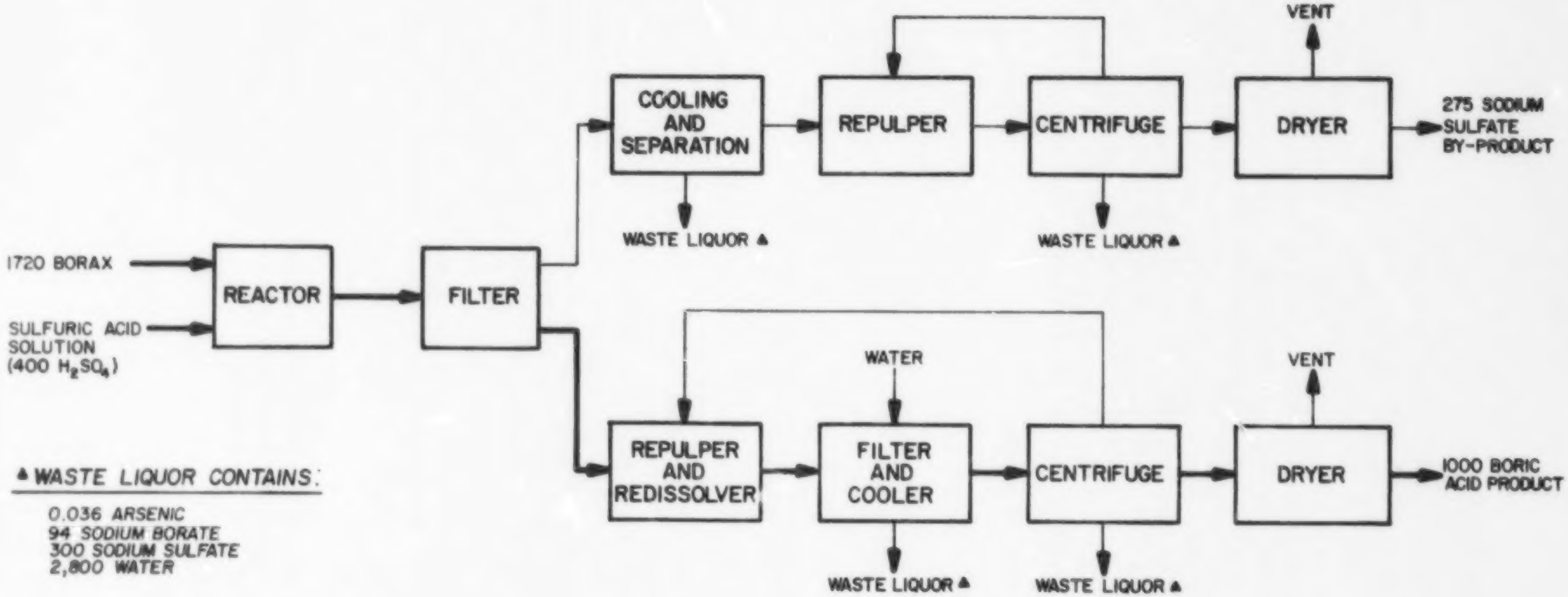


FIGURE 5-38
BORIC ACID MANUFACTURE

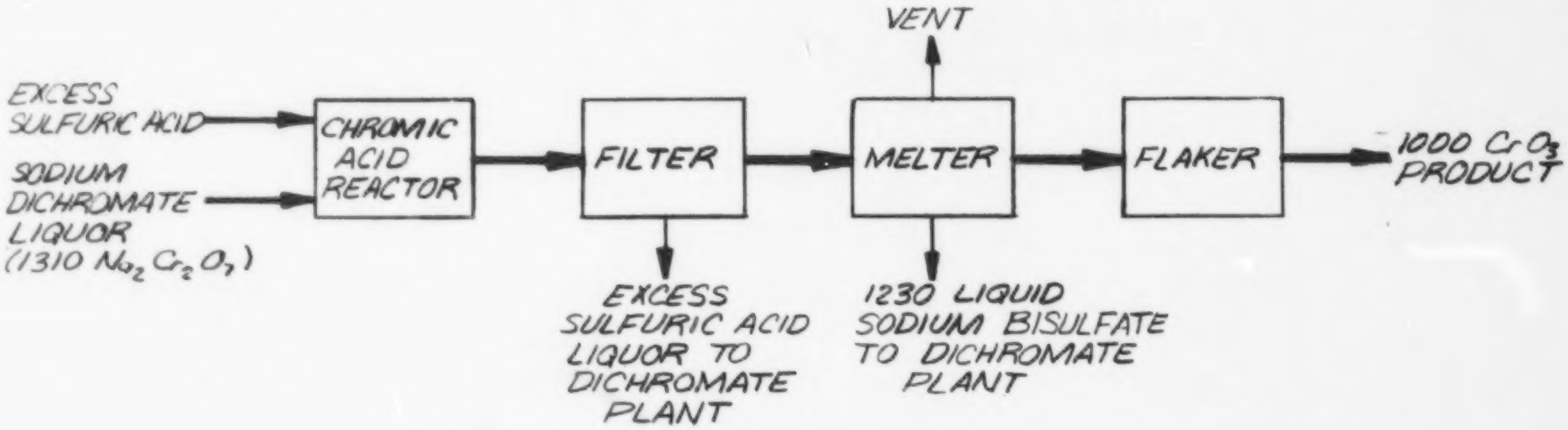

EXCESS SULFURIC ACID
SODIUM DICHROMATE LIQUOR (1310 $Na_2Cr_2O_7$)
CHROMIC ACID REACTOR
FILTER
EXCESS SULFURIC ACID LIQUOR TO DICHROMATE PLANT
VENT
MELTER
1230 LIQUID SODIUM BISULFATE TO DICHROMATE PLANT
FLAKER
1000 CrO_3 PRODUCT

FIGURE 5-39
CHROMIC ACID MANUFACTURE

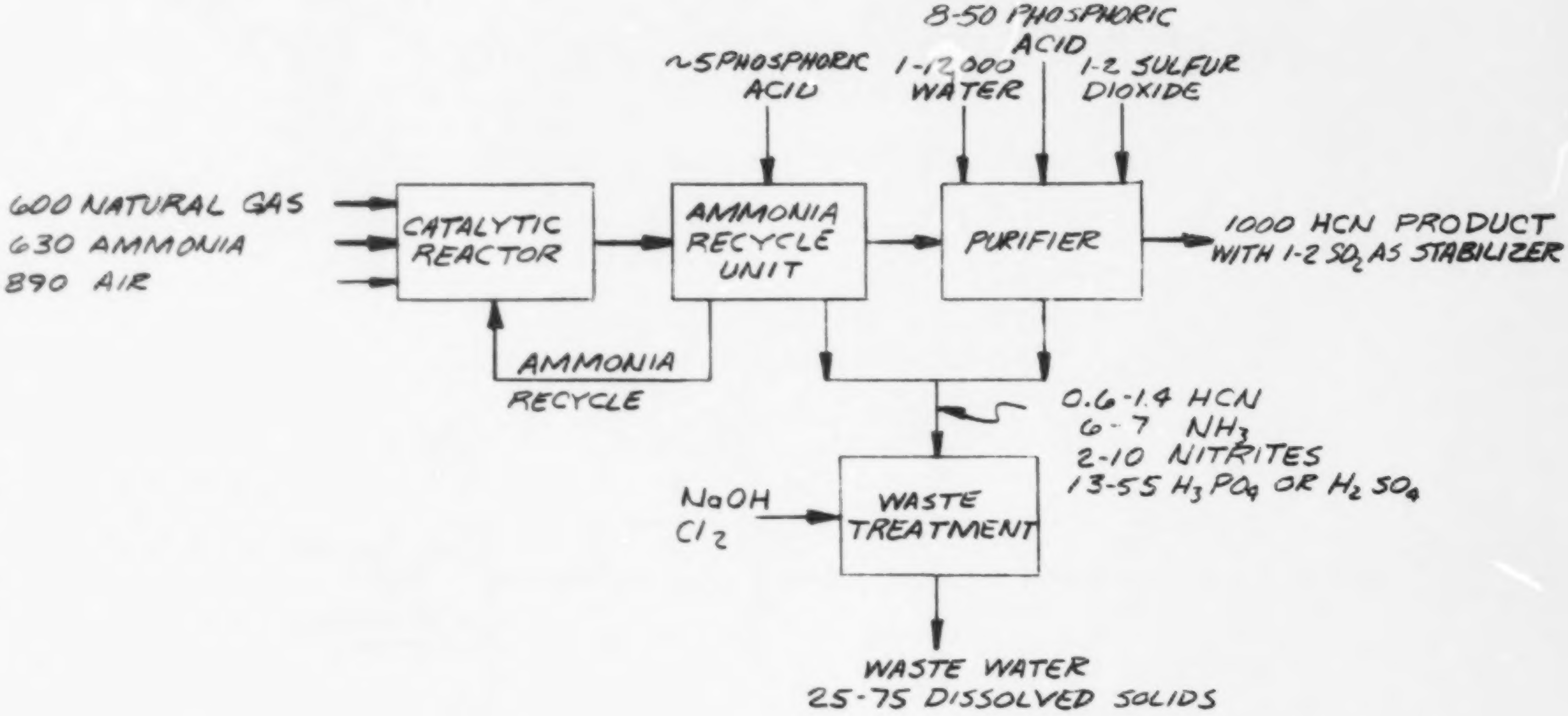


FIGURE 5-40
HYDROGEN CYANIDE MANUFACTURE BY THE ANDRUSSOW PROCESS

5.5.2.5 Hydrofluoric Acid

This material is made by the reaction of fluorspar (CaF_2) with concentrated sulfuric acid in a furnace. The hydrofluoric acid leaves the furnace as a gas, which is then cooled and absorbed in water prior to purification. In the purification system, the crude acid is redistilled and either absorbed in water to yield aqueous hydrofluoric acid or compressed and bottled as anhydrous acid. Final drying of the anhydrous gas is accomplished with concentrated sulfuric acid. This process is shown in Figure 5-41. There are large amounts of co-product gypsum contaminated with fluorides which occur as a waste. This material is generally slurried and pumped to lagoons where lime is added to precipitate CaF_2 and neutralize any acid present. The waste water is then either discharged or recycled. These wastes closely resemble others from phosphorus production in terms of the fluoride problems encountered.

The concentration of CaF_2 in the solid waste from HF production is sufficient to render the toxicological properties of the total waste very similar to the properties of CaF_2 described in Appendix A. The leachate from the CaF_2-containing waste will exceed water quality standards. Furthermore, the leaching of high concentrations of fluoride ion (above 10 ppm and as high as 1,000 ppm) is possible by contacting with leach water of low pH and particularly with solutions of mineral acids, as may easily occur in an industrial landfill used over a long period of time. See Appendix A, Figure 1 for data on release of fluoride by acid contact. This additional potential hazard, together with the substantial present hazard to drinking water quality, is judged to be sufficient to regard these waste streams as hazardous although the material, calcium fluoride, is itself in the "moderately hazardous" category.

5.5.2.6 Chlorosulfonic Acid

Chlorosulfonic acid is manufactured by the reaction of sulfur trioxide and hydrogen chloride. The only wastes arise from the scrubbing of vent gases, and consist of dilute solutions of alkali metal salts which are discharged as waterborne wastes. No hazardous wastes are involved. The flow diagram is given in Figure 5-42.

5.5.2.7 Aggregate of SIC 28194 Hazardous Wastes

The only currently land-disposed hazardous wastes from SIC 28194 are the fluoride-contaminated wastes from hydrofluoric acid manufacture. Table 5-9 gives the water stream amounts (dry basis) and fluoride content on a state-by-

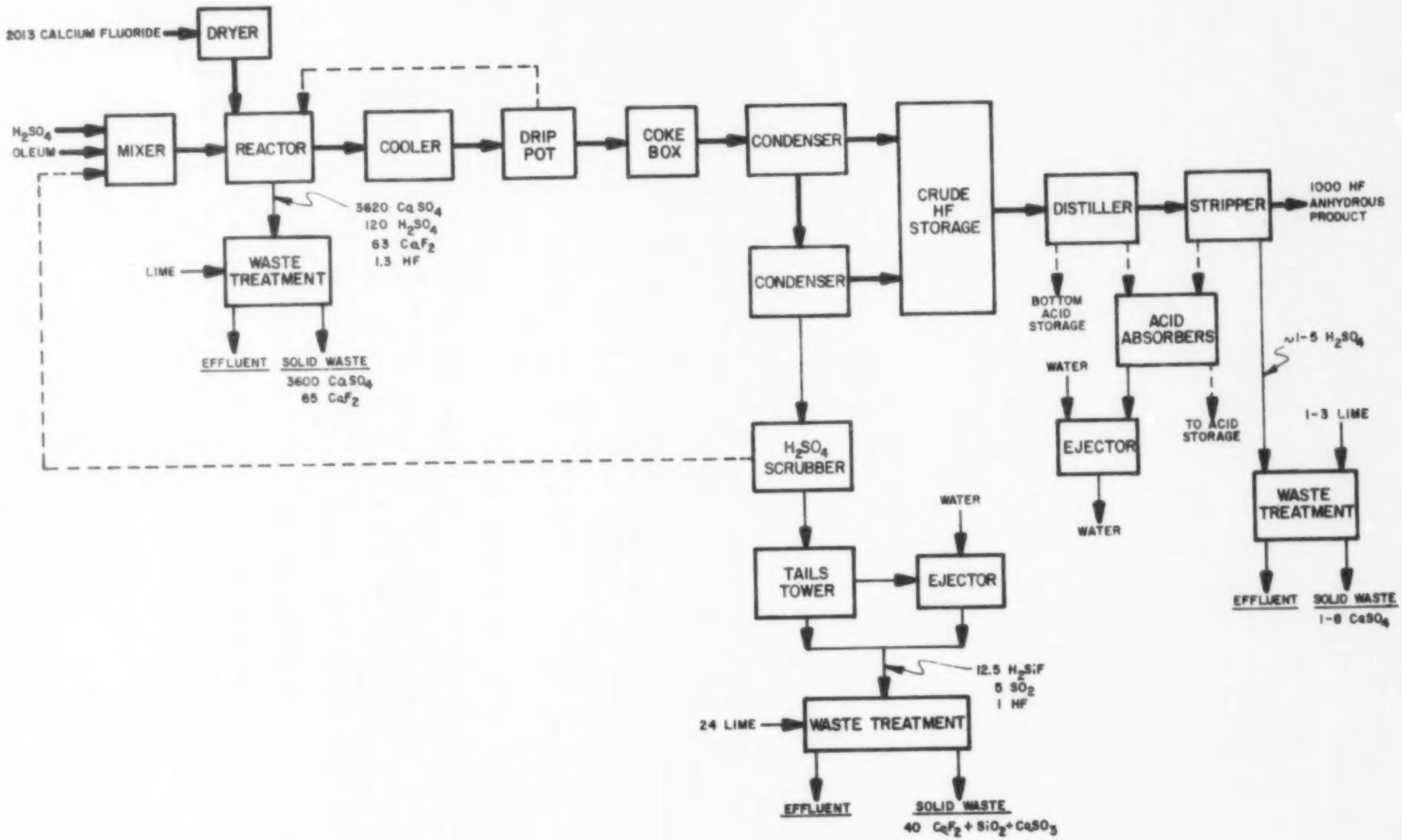


FIGURE 5-41
HYDROFLUORIC ACID MANUFACTURE

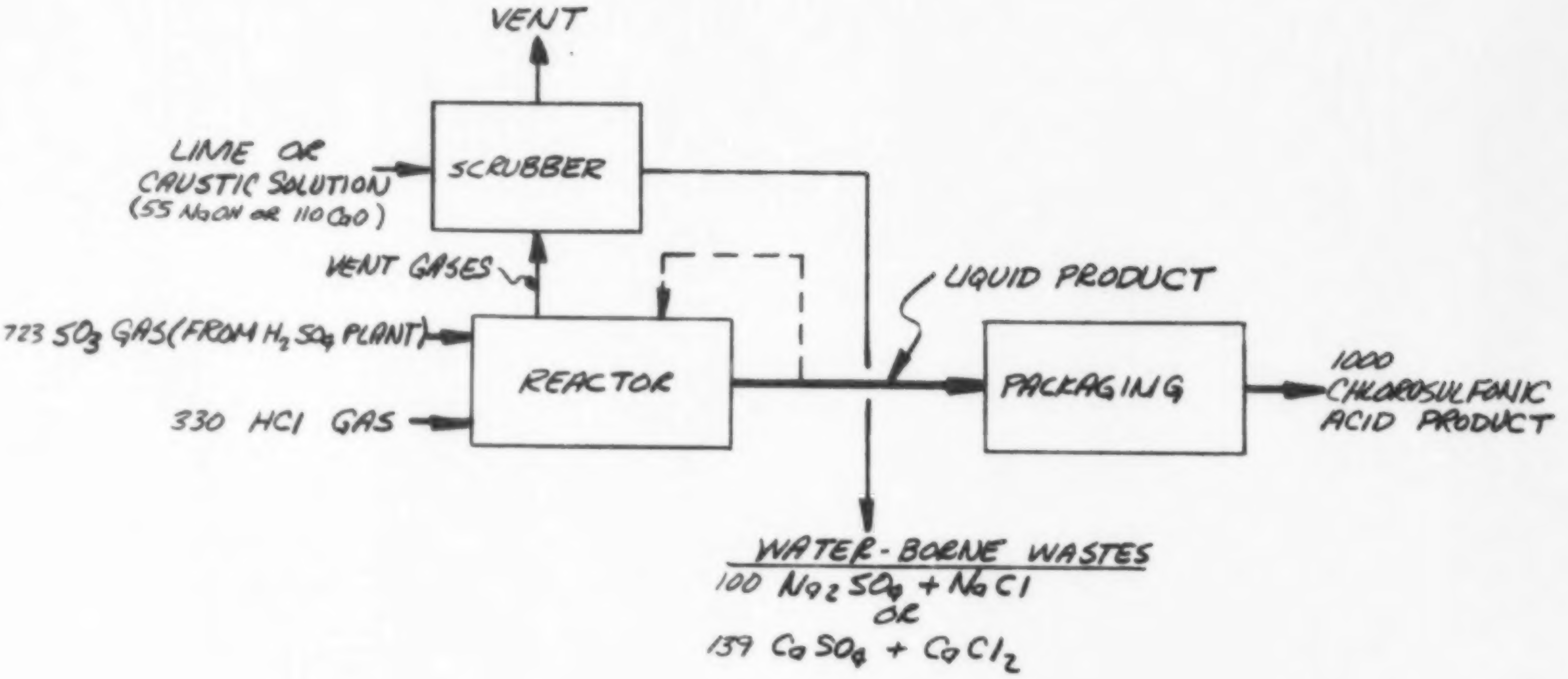


FIGURE 5-42

CHLOROSULFONIC ACID MANUFACTURE

Table 5-9. Hazardous Wastes Destined for Land Disposal from the SIC 28194 Inorganic Acids Industries (metric tons per year, dry basis)

		Current		1977			1983		
		Total Hazardous Wastes	Fluoride Content	Total Hazardous Wastes	Fluoride Content	Arsenic Content	Total Hazardous Wastes	Fluoride Content	Arsenic Content
IV	Alabama								
X	Alaska								
IX	Arizona								
VI	Arkansas								
IX	California	40,000	550	50,000	620	2.6*	65,000	820	2.9*
VIII	Colorado								
I	Connecticut								
III	Delaware	84,000	1,200	94,000	1,300		120,000	1,600	
IV	Florida								
IV	Georgia								
IX	Hawaii								
X	Idaho								
V	Illinois	49,000	670	54,000	750		69,000	750	
V	Indiana								
VII	Iowa								
VII	Kansas								
IV	Kentucky	84,000	1,200	94,000	1,300		120,000	1,600	
VI	Louisiana	350,000	4,900	400,000	5,500		500,000	6,900	
I	Maine								
III	Maryland								
I	Massachusetts								
V	Michigan								
V	Minnesota								
IV	Mississippi								
VII	Missouri								
VIII	Montana								
VII	Nebraska								
IX	Nevada								
I	New Hampshire								
II	New Jersey	37,000	510	42,000	580		53,000	720	
VI	New Mexico								
II	New York								
IV	North Carolina								
VIII	North Dakota								
V	Ohio	60,000	830	68,000	930		86,000	1,200	
VI	Oklahoma								
X	Oregon								
III	Pennsylvania	17,000	240	19,000	260		24,000	330	
I	Rhode Island								
IV	South Carolina								
VIII	South Dakota								
IV	Tennessee								
VI	Texas	580,000	8,000	660,000	9,000		830,000	11,000	
VIII	Utah								
I	Vermont								
III	Virginia								
X	Washington								
III	West Virginia	67,000	920	76,000	1,000		96,000	1,300	
V	Wisconsin								
VIII	Wyoming								
TOTAL		1,400,000	19,000	1,600,000	21,000	2.6*	2,000,000	26,000	2.9*
Region I									
II		37,000	510	42,000	580		53,000	720	
III		170,000	2,400	190,000	2,600		240,000	3,200	
IV		84,000	1,200	94,000	1,300		120,000	1,600	
V		109,000	1,500	120,000	1,700		160,000	2,000	
VI		930,000	13,000	1,100,000	14,000		1,300,000	18,000	
VII									
VIII									
IX		40,000	550	50,000	620	2.6*	65,000	820	2.9*
X									

*Arsenic-containing wastes generated by boric acid manufacture only. Total wastes from this segment 4,900 in 1977 and 6,400 in 1983.

state, regional, and national basis. The values given are based on both manufacturer supplied data and our estimates. The overall reliability is judged to be about 30%.

5.5.2.8 Projection of SIC 28194 Hazardous Wastes

By 1977, the effluent discharge limitations should cause arsenic-containing solid wastes from boric acid manufacture to be disposed of on land. No other process changes or treatments to reduce discharges are expected in this category which would affect land-disposed hazardous waste levels through 1983. The estimated production growth in both boric and hydrofluoric acid will probably average 4 percent per year in this period. The projections for 1977 and 1983 for SIC 28194 are given in Tables 5-9.

The overall trends for the amounts of hazardous wastes from SIC 28194 destined for land disposal in terms of metric tons per year (short tons per year) are summarized as:

Period	Current	1977	1983
dry basis	1.4×10^6 (1.5×10^6)	1.6×10^6 (1.7×10^6)	2.0×10^6 (2.2×10^6)
moisture included	1.9×10^6 (2.1×10^6)	2.1×10^6 (2.3×10^6)	2.7×10^6 (2.9×10^6)

It should be noted that this subcategory is responsible for approximately 70% of the hazardous waste tonnage generated by the inorganic chemicals industry.

5.5.3 Aluminum Oxide and Aluminum Hydroxide (SIC 28195)

These two materials are produced from bauxite by the process shown in Figure 5-43. The raw bauxite ore is first reacted with alkali under pressure to yield a sodium aluminate solution. The insolubles (red muds) are separated from this and discarded, and the solutions are then decomposed by dilution to yield an alumina trihydrate (aluminum hydroxide) which is then recovered by filtration and dried.

The pure oxide is prepared from this material by calcination. There are numerous wastes coming from this process. These include:

(1) The ore residues ("red muds") which consist of silica and iron oxides contaminated with spent caustic. These are generally neutralized prior to disposal and are non-hazardous in their final form.

(2) The spent weak caustic resulting from decomposition of the sodium aluminate liquors. This is a water-borne waste stream which is either reconcentrated and reused or neutralized prior to discharge.

(3) Dusts from calcination operations. These are chiefly alumina and are recycled.

The flow diagram of Figure 5-43 is constructed with the latter two streams internally recycled.

5.5.3.1 Aggregate of SIC 28195 Hazardous Wastes

No hazardous wastes destined for land disposal are currently generated in this industry segment.

5.5.3.2 Projection of SIC 28195 Hazardous Wastes

In the period through 1983, no process changes or treatments to reduce air or water discharges are expected to cause any hazardous wastes to be generated for land disposal.

5.5.4 Other Aluminum Compounds (SIC 28196)

5.5.4.1 Aluminum Chloride

The flow diagram for the principal process is given in Figure 5-44. The anhydrous material is prepared by reaction of chlorine with molten aluminum metal. The product $AlCl_3$ sublimes and is condensed from the gas phase and recovered as a product. Most of the wastes are airborne and consist of unreacted chlorine and uncollected $AlCl_3$. Dry and wet collection methods used in the industry recover much of the uncollected product. In some cases this is subsequently converted to a solution grade product, while in others, both the chlorine and $AlCl_3$ wastes are removed from the vent gases by wet scrubbing with alkali solutions leading to a discharge of a water-borne waste. The unreacted aluminum metal is the only solid waste generated here and it is not hazardous. Some high purity hydrated aluminum chloride is also produced by reaction of alumina with HCl. The resulting solution is then evaporated to recover a solid product. All wastes in this case are water-borne arising from the use of barometric condensers and are neither hazardous, nor disposed of on land.

5.5.4.2 Aluminum Fluoride

AlF_3 is produced, as shown in Figure 5-45, by the reaction of alumina with hydrofluoric acid. The hydrated alumina and anhydrous hydrofluoric acid are added to a reactor. The solid product is cooled collected, and readied for shipment.

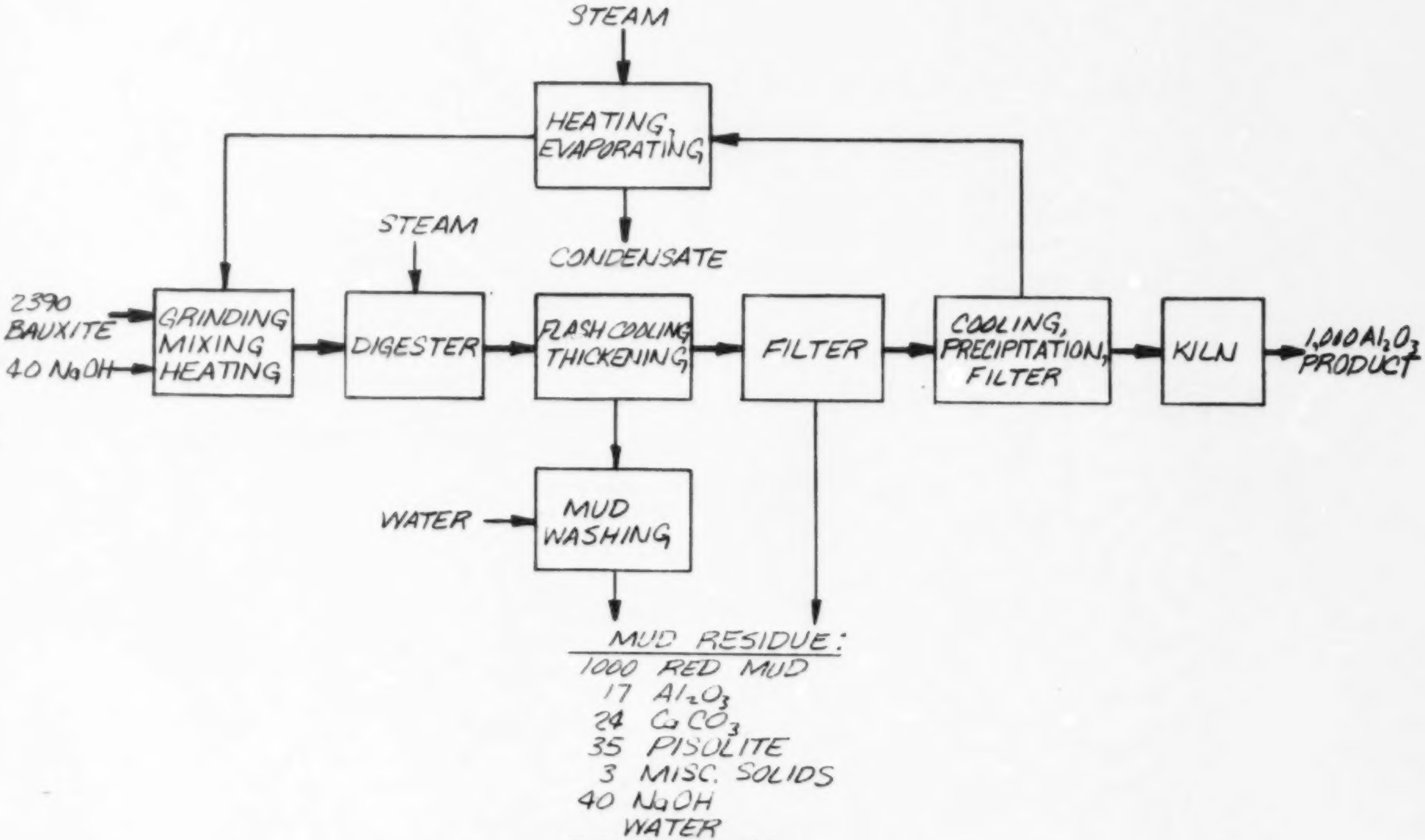


FIGURE 5-43

ALUMINA MANUFACTURE FROM BAUXITE

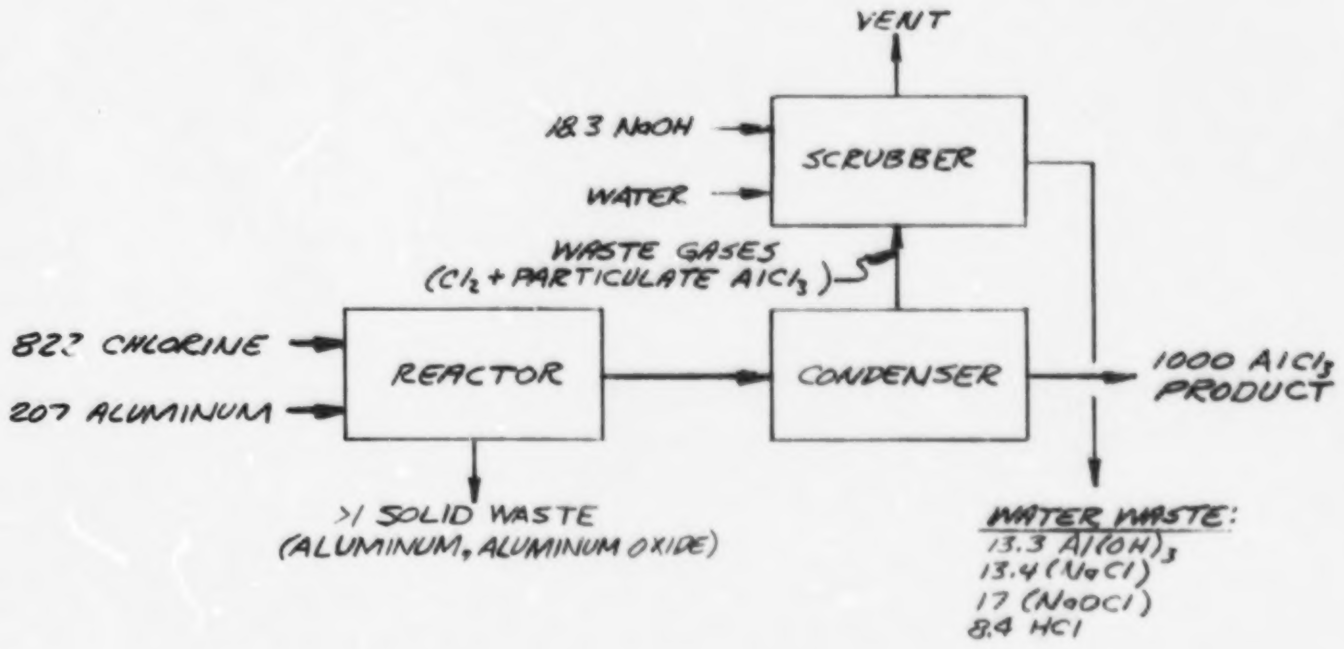


FIGURE 5-44
ALUMINUM CHLORIDE MANUFACTURE

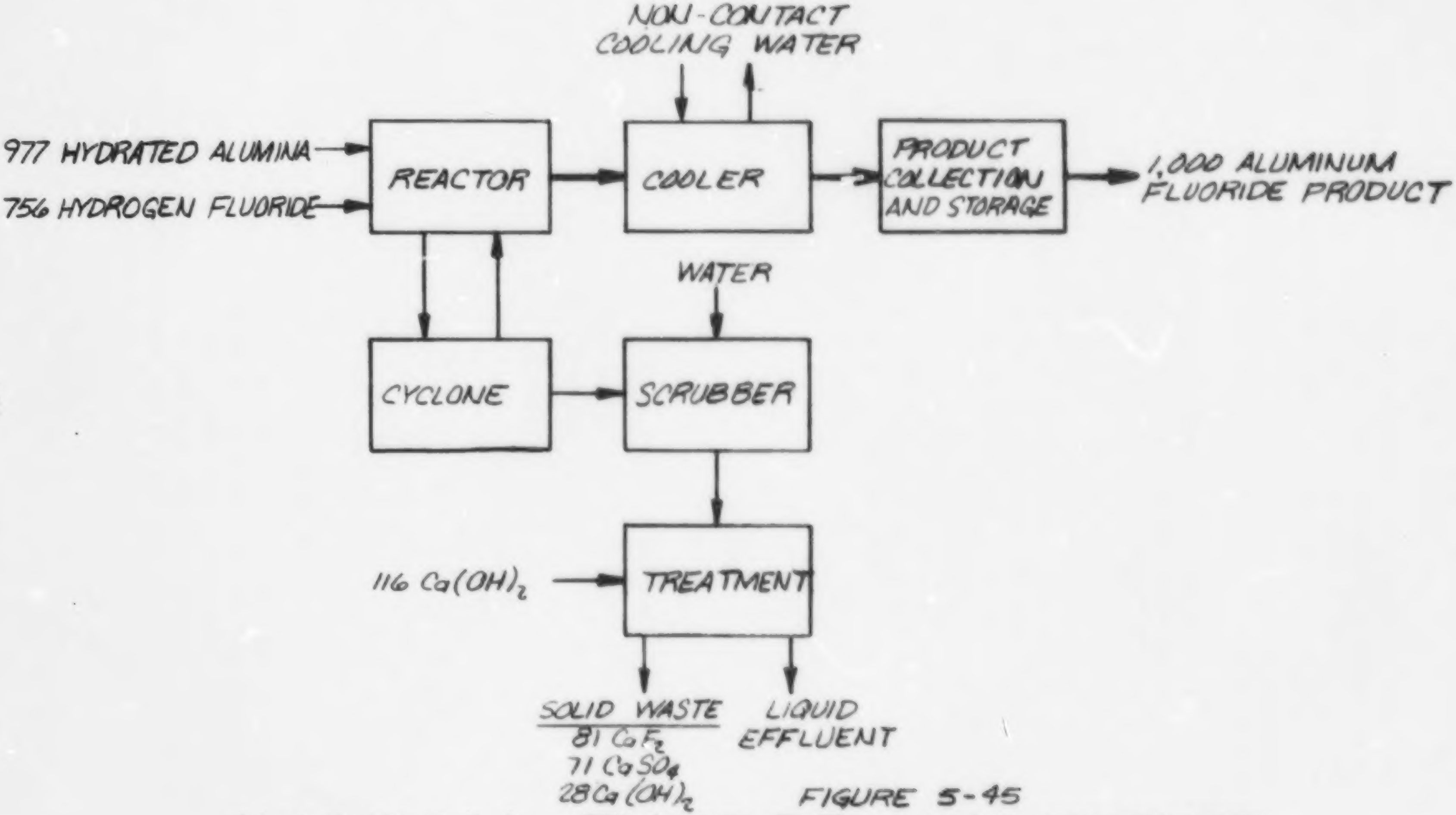


FIGURE 5-45

ALUMINUM FLUORIDE MANUFACTURE

In some plants the reaction takes place in aqueous solution, from which the water must be driven off to effect recovery of the solid product. All of the wastes arise from the scrubbing of vent gases, and the waste waters generated (for the three facilities producing this product) are either discharged without treatment or treated in conjunction with other waste streams.

The solid waste generated by waste water treatment consists of calcium hydroxide and calcium sulfate, neither of which are hazardous, and calcium fluoride which is a hazardous constituent. The concentration of CaF_2 as fluoride in the waste is about 20 percent (w/w dry basis), thus rendering the overall biological properties of the waste similar to those described in Appendix A for CaF_2. Protection against contamination of ground and surface waters is required, for leaching can develop fluoride concentration in excess of drinking water standards. Furthermore, the leaching of high concentrations of fluoride ion (above 10 ppm and as high as 1,000 ppm) is possible by contacting with leach water of low pH and particularly with solutions of mineral acids, as may easily occur in an industrial landfill used over a long period of time. See Appendix A, Figure 1 for data on release of fluoride by acid contact. This additional potential hazard, together with the substantial present hazard to drinking water quality, is judged to be sufficient to regard these waste streams as hazardous although the material, calcium fluoride, is itself in the "moderately hazardous" category.

5.5.4.3 Aluminum Sulfate

As shown in Figure 5-46, alum (aluminum sulfate) is produced by reaction of alumina, bauxite, or clay with sulfuric acid. Ground ore and acid are reacted in a digester, from which the products, aluminum sulfate in solution plus muds and other insoluble materials from the ore, are then fed into a settling tank. The aluminum sulfate solution is then clarified and filtered to remove any remaining insolubles. This may be used as solution or evaporated to yield a solid product. There are solid wastes consisting of ore residues (silica, etc.), but these are extremely insoluble materials of a non-hazardous nature.

5.5.4.4 Aggregate of SIC 28196 Hazardous Wastes

The only SIC 28196 process generating hazardous wastes destined for land disposal is that for the manufacture of aluminum fluoride. The waste stream is fluoride-containing gypsum and lime, which is similar to the hazardous waste stream from hydrofluoric acid manufacture (SIC 28195)

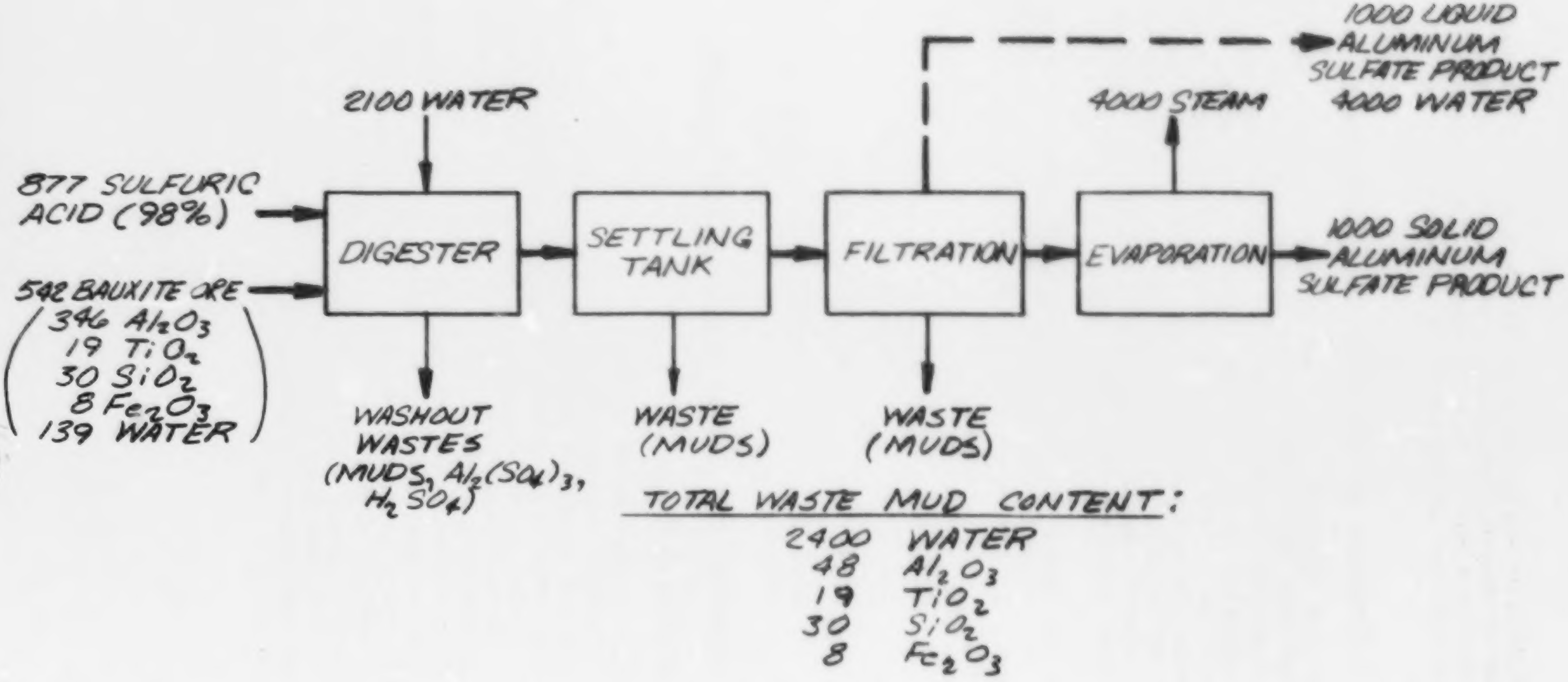


FIGURE 5-46

ALUMINUM SULFATE MANUFACTURE

discussed earlier. Table 5-10 lists the current situation on a state-by-state, regional, and national basis. The values given are based on both manufacture-supplied data and our estimates, and is expected to be accurate to within 30 percent.

5.5.4.5 Projection of SIC 28196 Hazardous Wastes

For the period through 1983, no process changes are anticipated that will affect the hazardous wastes destined for land disposal in SIC 28196. A minor effect will ensue with the imposition of air and water regulations, since the largest portion of the fluoride waste is already removed to land disposal by treatment. Table 5-10 also gives the projected situations in 1977 and 1983. The growth in aluminum flouride manufacture is estimated to average 4 percent per year through this period.

The trends in hazardous wastes for land disposal from SIC 28196 can thus by summarized as below. The values are total amounts in terms of metric tons per year (short tons per year):

Period	Current	1977	1983
dry basis	32,000 (35,000)	37,000 (41,000)	40,000 (44,000)
moisture included	43,000 (47,000)	49,000 (54,000)	53,000 (59,000)

5.5.5 Potassium and Sodium Compounds (SIC 28197)

5.5.5.1 Potassium Metal

This material is produced by reaction of sodium metal with potassium chloride vapors as shown in Figure 5-47. The molten potassium chloride flows over Raschig rings in the packed column, where it contacts ascending sodium vapors coming from a gas-fired reboiler. An equilibrium is established between the two, yielding sodium chloride and elemental potassium. The sodium chloride formed is continuously withdrawn at the base of the apparatus and may be sold. The column operating conditions may be varied to yield either pure potsssium metal as an overhead product or to vaporize sodium along with the potassium to produce sodium-potassium (NaK) alloys of varying compositions. According to the one manufacturer of this chemical in the U.S., the sodium chloride co-product is utilized at the same facility and is not a waste. There are no other wastes involved.

Table 5-10. Hazardous Wastes Destined for Land Disposal from the SIC 28196 Aluminum Compounds Industries (metric tons per year, dry basis)

		Current		1977		1983	
		Total Hazardous Wastes	Fluoride Content	Total Hazardous Wastes	Fluoride Content	Total Hazardous Wastes	Fluoride Content
IV	Alabama						
X	Alaska						
IX	Arizona						
VI	Arkansas						
IX	California						
VIII	Colorado						
I	Connecticut						
III	Delaware						
IV	Florida	3,200	800	3,600	900	4,100	1,000
IV	Georgia						
IX	Hawaii						
X	Idaho						
V	Illinois						
V	Indiana						
VII	Iowa						
VII	Kansas						
IV	Kentucky						
VI	Louisiana	14,000	3,500	16,000	3,900	17,000	4,400
I	Maine						
III	Maryland						
I	Massachusetts						
V	Michigan						
V	Minnesota						
IV	Mississippi						
VII	Missouri						
VIII	Montana						
VII	Nebraska						
IX	Nevada						
I	New Hampshire						
II	New Jersey						
VI	New Mexico						
II	New York						
IV	North Carolina						
VIII	North Dakota						
V	Ohio						
VI	Oklahoma	3,200	800	3,600	900	4,100	1,000
X	Oregon						
III	Pennsylvania						
I	Rhode Island						
IV	South Carolina						
VIII	South Dakota						
IV	Tennessee						
VI	Texas	12,000	3,000	14,000	3,400	15,000	3,800
VIII	Utah						
I	Vermont						
III	Virginia						
X	Washington						
III	West Virginia						
V	Wisconsin						
VIII	Wyoming						
TOTAL		32,000	8,100	37,000	9,100	40,000	10,200
Region I							
II							
III							
IV		3,200	800	3,600	900	4,100	1,000
V							
VI		29,000	7,300	34,000	8,200	36,000	9,200
VII							
VIII							
IX							
X							

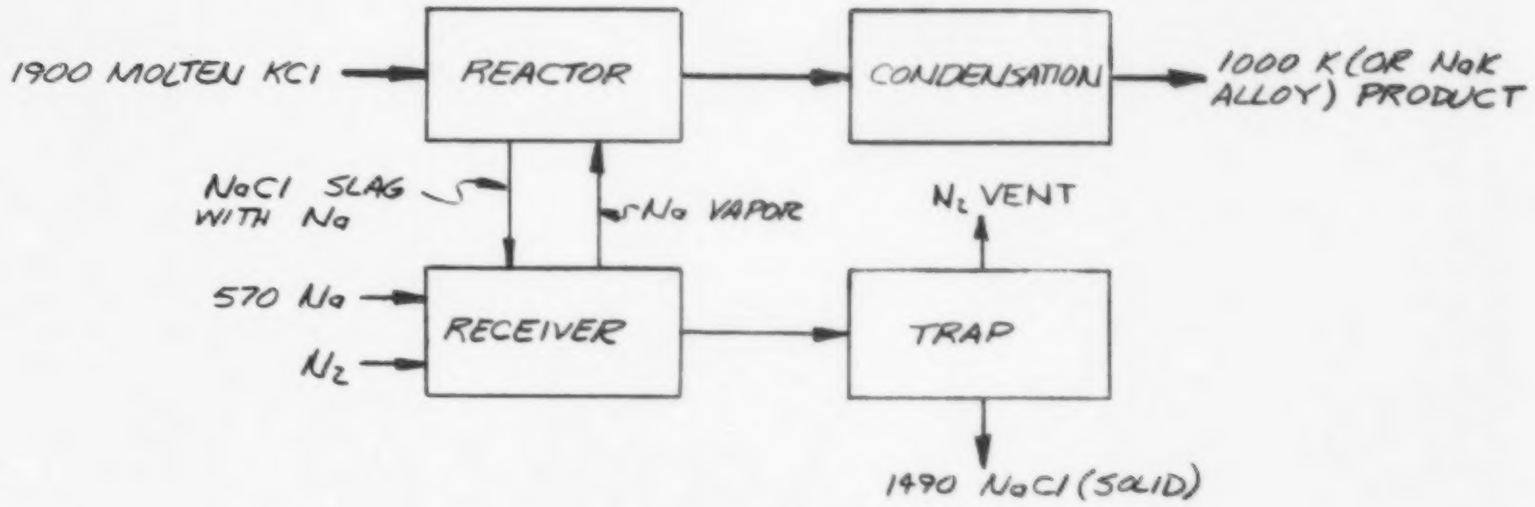


FIGURE 5-47
POTASSIUM MANUFACTURE

5.5.5.2 Potassium Sulfate

This product is produced by the reaction in solution of potassium chloride with langbeinite ore ($K_2SO_4.MgSO_4$), as shown in Figure 5-48. Mined langbeinite is crushed and dissolved in water to which potassium chloride is added. Partial evaporation of the solution results in selective precipitation of potassium sulfate which is recovered by centrifugation or filtration, dried, and sold. The remaining brine liquor is either discharged to an evaporation pond, reused as process water, or evaporated. Sodium chloride impurities in the ore and, in many cases, the $MgCl_2$ co-product, are the only waste products. These exit the plant in the form of brine solutions which are fed to evaporation ponds. All of this material is produced close to areas where it is mined (in New Mexico) and the solids generated by evaporation are not hazardous (i.e., sodium and magnesium chlorides).

5.5.5.3 Potassium Iodide

As shown in Figure 5-49, this chemical is produced, by reaction of iodine with potassium hydroxide. The iodate precipitates out and is removed as a by-product. The iodide solution is evaporated to dryness and fused in a gas-fired furnace to decompose residual iodate. The fused iodide is redissolved in distilled water, and barium carbonate, hydrogen sulfide, ferrous iodide, and carbon dioxide gas are added to precipitate impurities and adjust the pH of the solution. The solution is filtered and fed to crystallizers, from which the potassium iodide crystals are centrifuged, dried, screened, and packaged. The mother liquor from the crystallizers is recycled. An iodate co-product is recovered, and there are small amounts of solid wastes generated by product purification steps. However, the quantities of these wastes are very small, and only two locations are involved. The solid wastes contain barium sulfate and small amounts of insoluble sulfides. Because of its virtually total insolubility in water and body fluids, barium sulfate is a nonhazardous waste constituent. Thus these waste streams are judged not to constitute a significant hazardous waste when land-disposed.

5.5.5.4 Potassium Chloride

This material is produced from natural brines and from sylvinite ores. In the former case there are no hazardous wastes for disposal since the spent brine is returned to the well, which constitutes recycle. In the sylvite process (which is shown in Figure 5-50), the ore is mined, crushed, screened, and wet-ground in brine to dissolve most of the

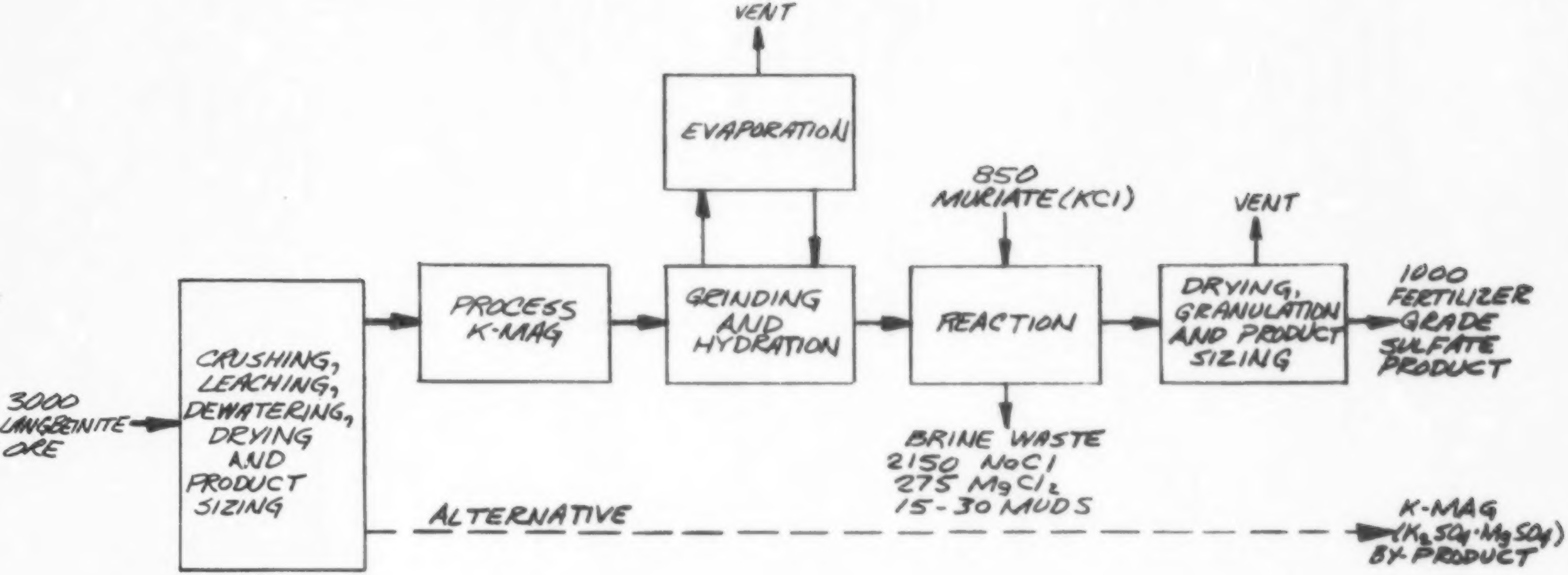


FIGURE 5-48
POTASSIUM SULFATE MANUFACTURE

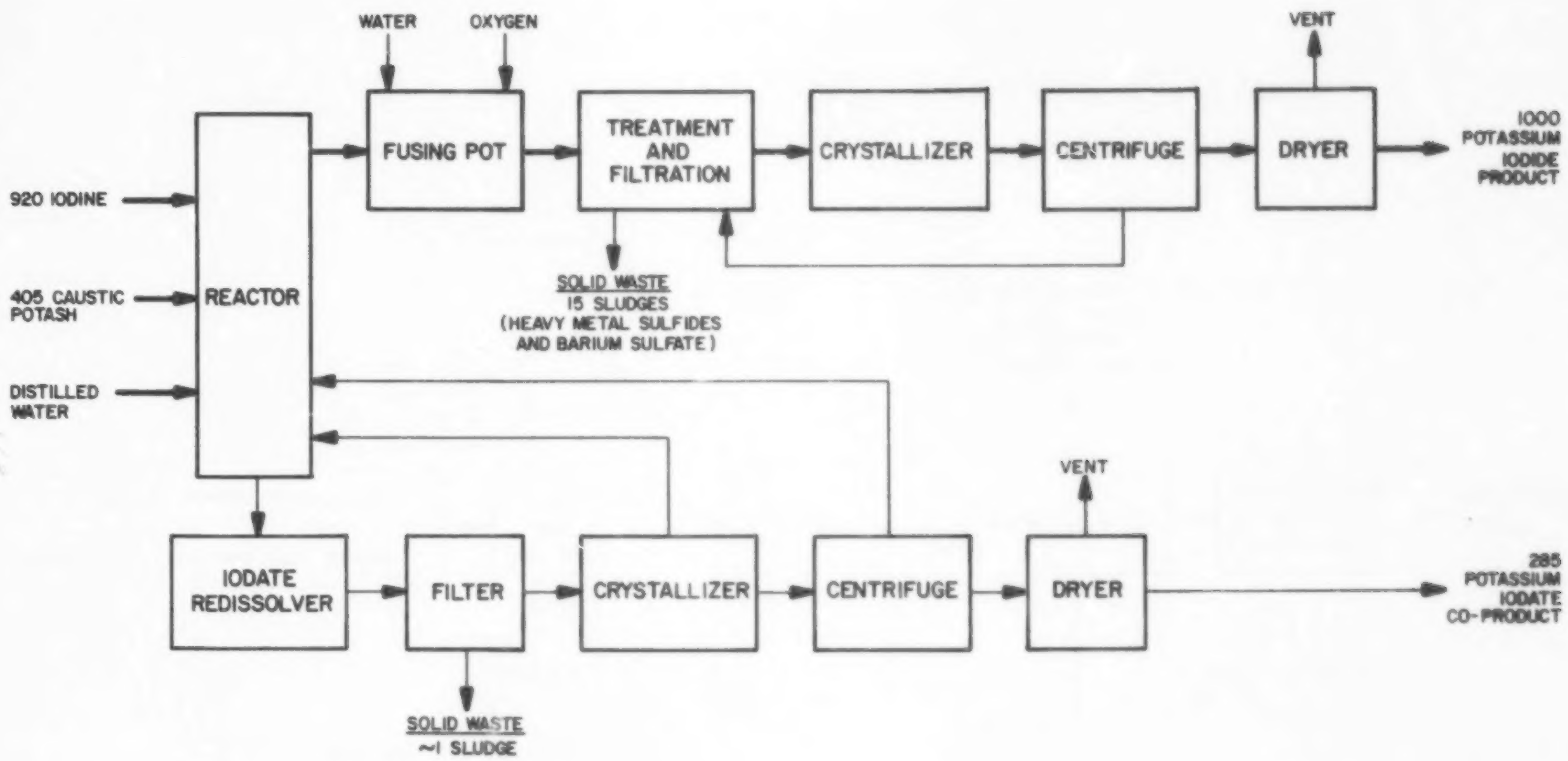


FIGURE 5-49
POTASSIUM IODIDE MANUFACTURE

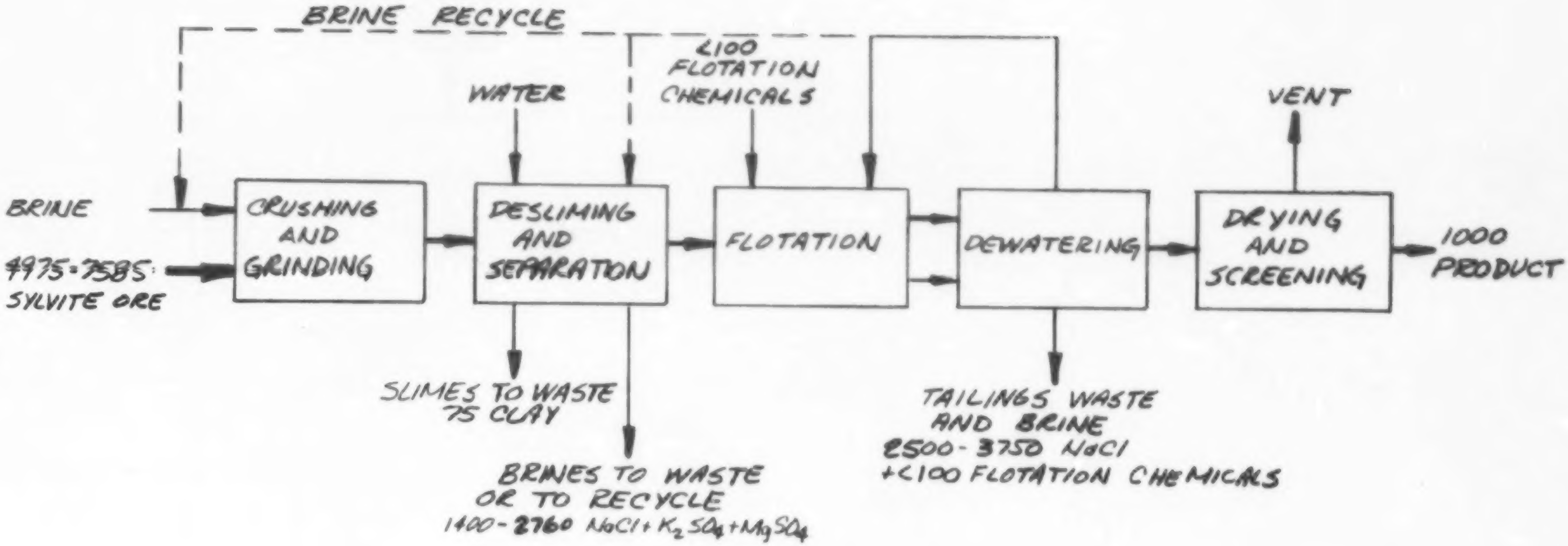


FIGURE 5-50

POTASSIUM CHLORIDE MANUFACTURE FROM SYLVITE ORE soluble salts. Clay is removed by settling, as are the other undissolved materials in a separate step. The brine, saturated in sodium chloride, is fed to a flotation cell where air is passed through the solution (to which flotation agents such as tallow amines, polyalkyl glycol, starch, etc. have been added) in order to carry sodium chloride into the froth. The potassium chloride brine is then vacuum-crystallized, and the potassium chloride crystalls are centrifuged, dried, screened and packaged. There are large amounts of waste generated due to the presence of sodium chloride and silica although these are not hazardous in these amounts at these locations. These wastes are slurried and fed to evaporation ponds and all processing this occurs in a sparsely populated arid region (New Mexico).

5.5.5.5 Borax (Sodium Tetraborate Decahydrate)

Borax is extracted either from Searles Lake brines or from natural ores. In the first case, there are no solid wastes produced. With ore extraction, however, there are ore residues produced which contain small amounts of a naturally-occurring arsenic sulfide mineral called "Realgar". It is chemically As_2S_2. Generally, these arsenic containing wastes are disposed of in lined evaporation ponds. The mining operations involve a single plant location in an arid and isolated area. The ore is crushed and conveyed to dissolvers where water and recycled mother liquor are added to dissolve the borax. The insolubles are settled out in ponds, and the clarified borax solution (mother liquor) is fed to crystallizers where a slurry of borax crystals in water is formed. The borax is separated from the water by centrifugation, dried, screened and packaged. The product borax is a hydrated sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$. For boric acid manufacture the pentahydrate, $Na_2B_4O_7 \cdot 5H_2O$, is produced. The flow diagram is shown in Figure 5-51.

The arsenic is present in the mine run ore and associated shales as "Realgar", a natural form of arsenic sulfide. The occurrence is intermittent, and a given ore horizon can vary from 0 to over 1000 ppm as arsenic. Because of low solubility, most of the Realgar remains in solid form and is deposited in ponds with clay.

Water and air discharges are already regulated by stringent state requirements. There is no likelihood of percolation into ground water because there is none in the area. Water in the ponds above the gangue material eliminates the possibility of blowing dust. Thus there is judged to be no

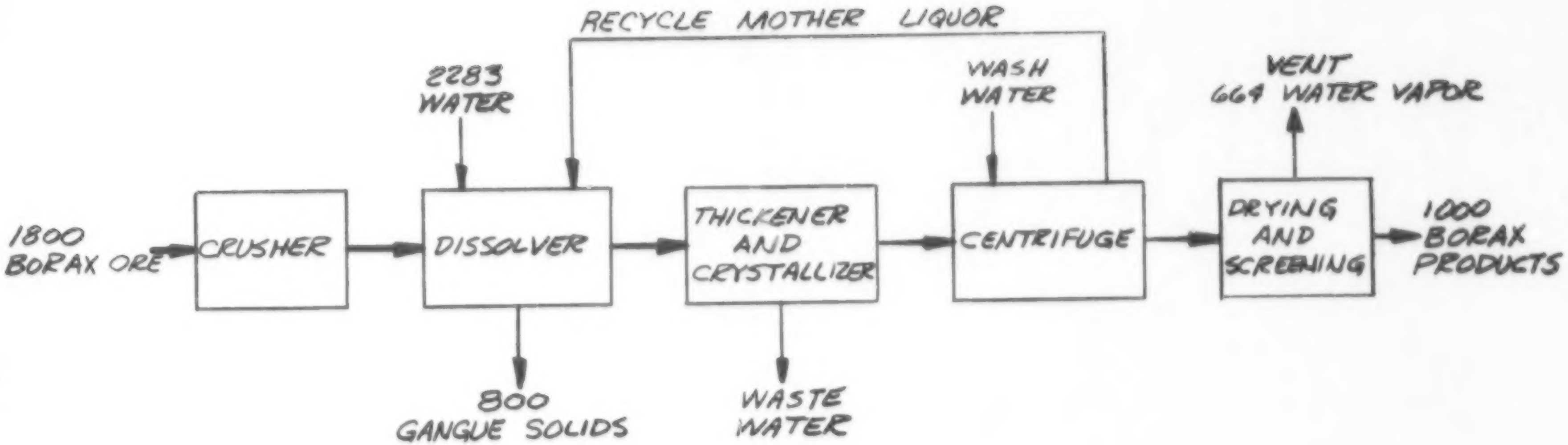


FIGURE 5-51

BORAX MANUFACTURE FROM ORE

environmental problem at this location due to the disposal of these ore wastes on land.

The total amounts of these wastes are very large, about 900,000 metric tons per year (1,000,000 short tons per year) on a dry basis containing approximately 45 ppm of arsenic as Realgar. Because of the localization of this industry, the natural mineral form of the waste, problem imposed, its waste stream will not be considered hazardous for the purpose of aggregation with the other SIC 28197 streams in this study.

5.5.5.6 Sodium Fluoride

This material is produced by two processes as shown in Figures 5-52 and 5-53. The first involves reaction of soda ash with hydrofluoric acid. Anhydrous hydrofluoric acid (hydrogen fluoride) and soda ash are reacted, and hydrogen fluoride fumes and carbon dioxide are scrubbed with a soda ash solution. The product from the reactor is a slurry of sodium fluoride which is vacuum filtered to recover the fluoride. The product is then dried and packaged. No wastes are generated in this process. The second involves recovery from impure phosphoric acid. Sodium silicofluoride is recovered and then converted to the fluoride by reaction with caustic soda. The wastes from this process are water-borne and contain silicates and fluorides. Wastewater treatment generates moderate amounts of calcium fluoride as a solid waste. Calcium fluoride, a moderately hazardous material, is the major constitutent of the waste stream, and the overall properties of the waste are the same as those described for the individual components (Appendix A). Protection against contamination of ground and surface waters is required. See Section 5.5.2.5 for detailed discussion of hazard.

5.5.5.7 Sodium Sulfide and Hydrosulfide

These products are made, as shown in Figure 5-54, by reaction of hydrogen sulfide with caustic soda. The wastes from this process are chiefly water-borne and contain sulfides. Depending on whether aeration or chemical precipitation is used to treat the wastewater, solid wastes may or may not be generated. For cases where they are, small amounts of iron sulfide are the solid waste. This waste is not hazardous.

5.5.5.8 Sodium Hydrosulfite

This material is made by two processes as shown in Figures 5-55 and 5-56. In the first, zinc and sulfur dioxide are reacted in solution to form zinc hydrosulfite. The

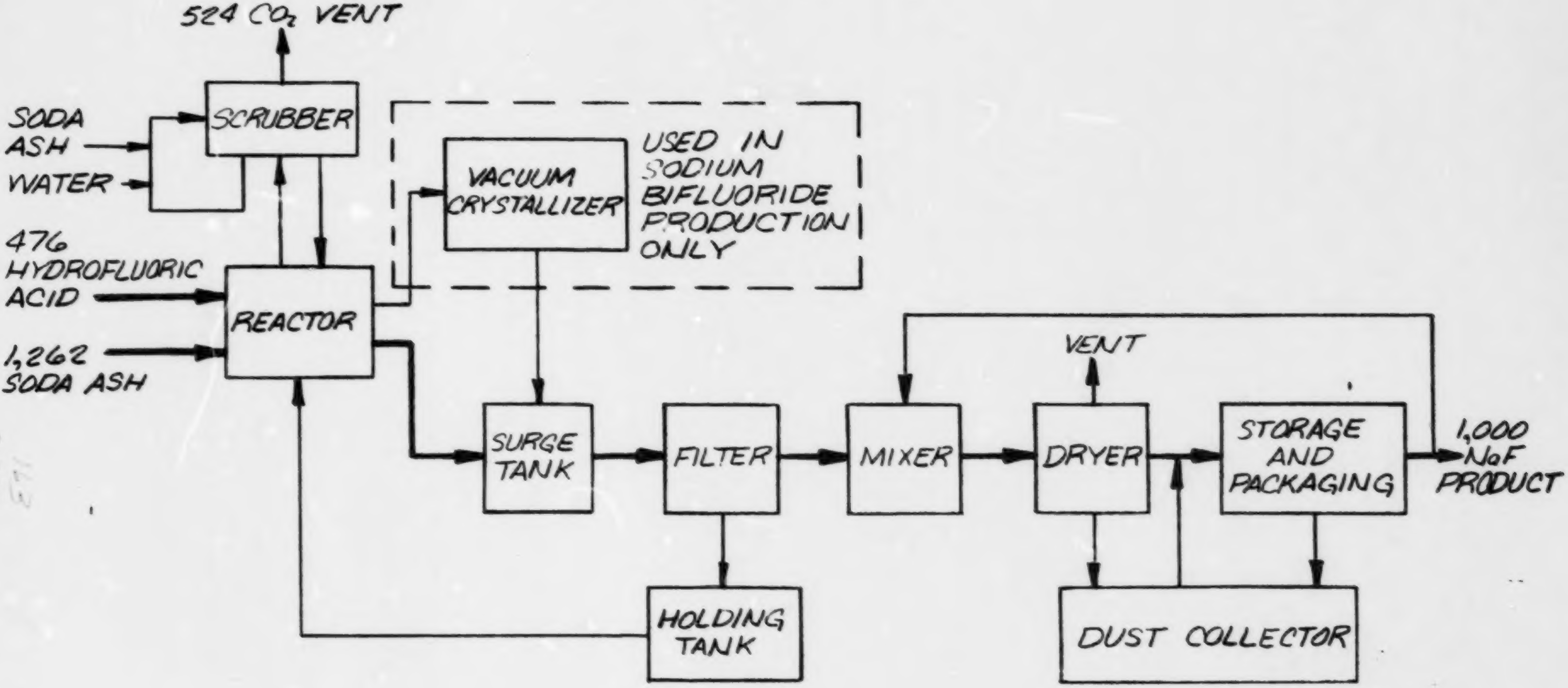


FIGURE 5-52
SODIUM FLUORIDE MANUFACTURE
FROM HYDROFLUORIC ACID

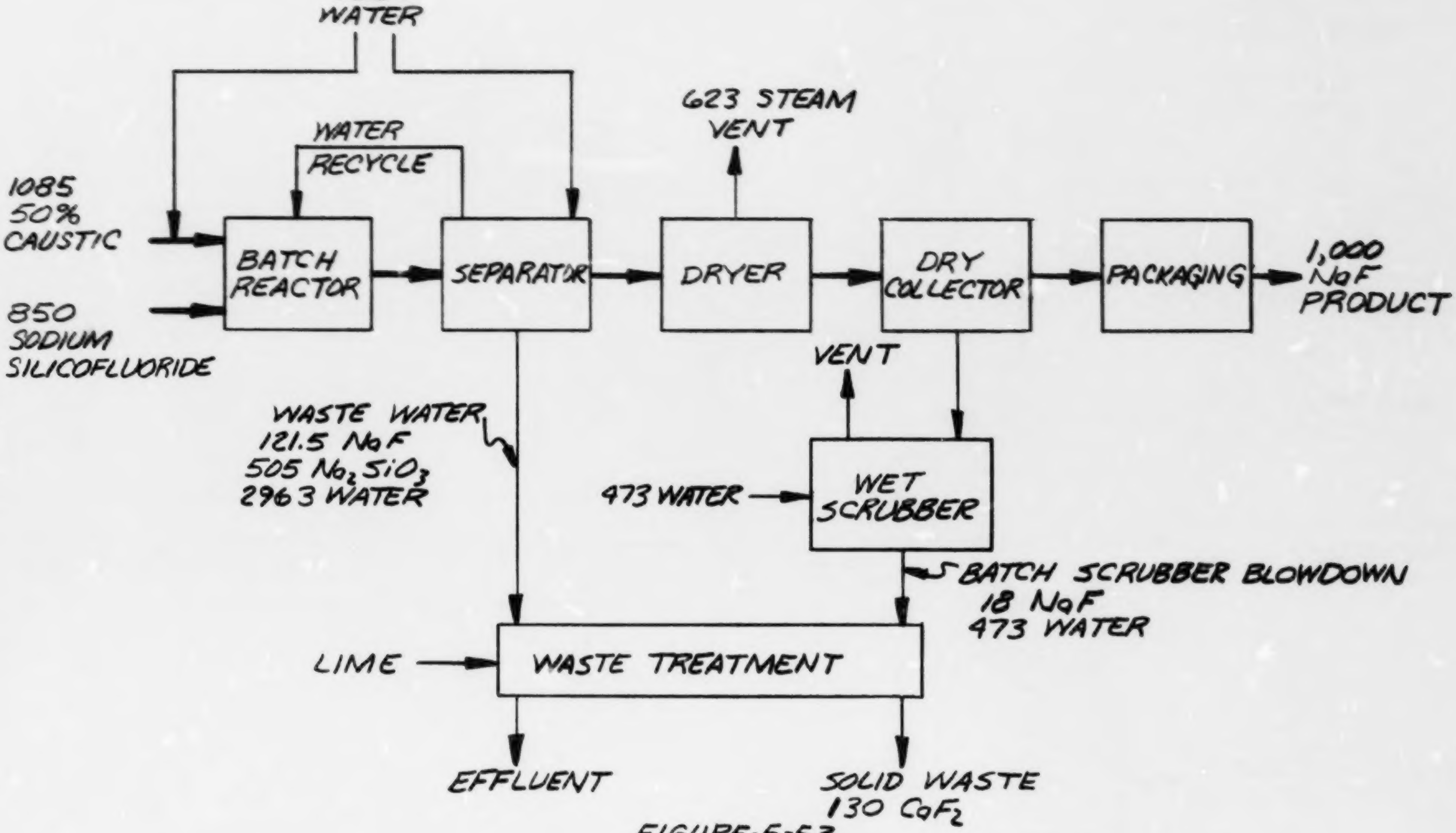


FIGURE-5-53

SODIUM FLUORIDE MANUFACTURE
FROM CAUSTIC SODA AND SODIUM SILICOFLUORIDE

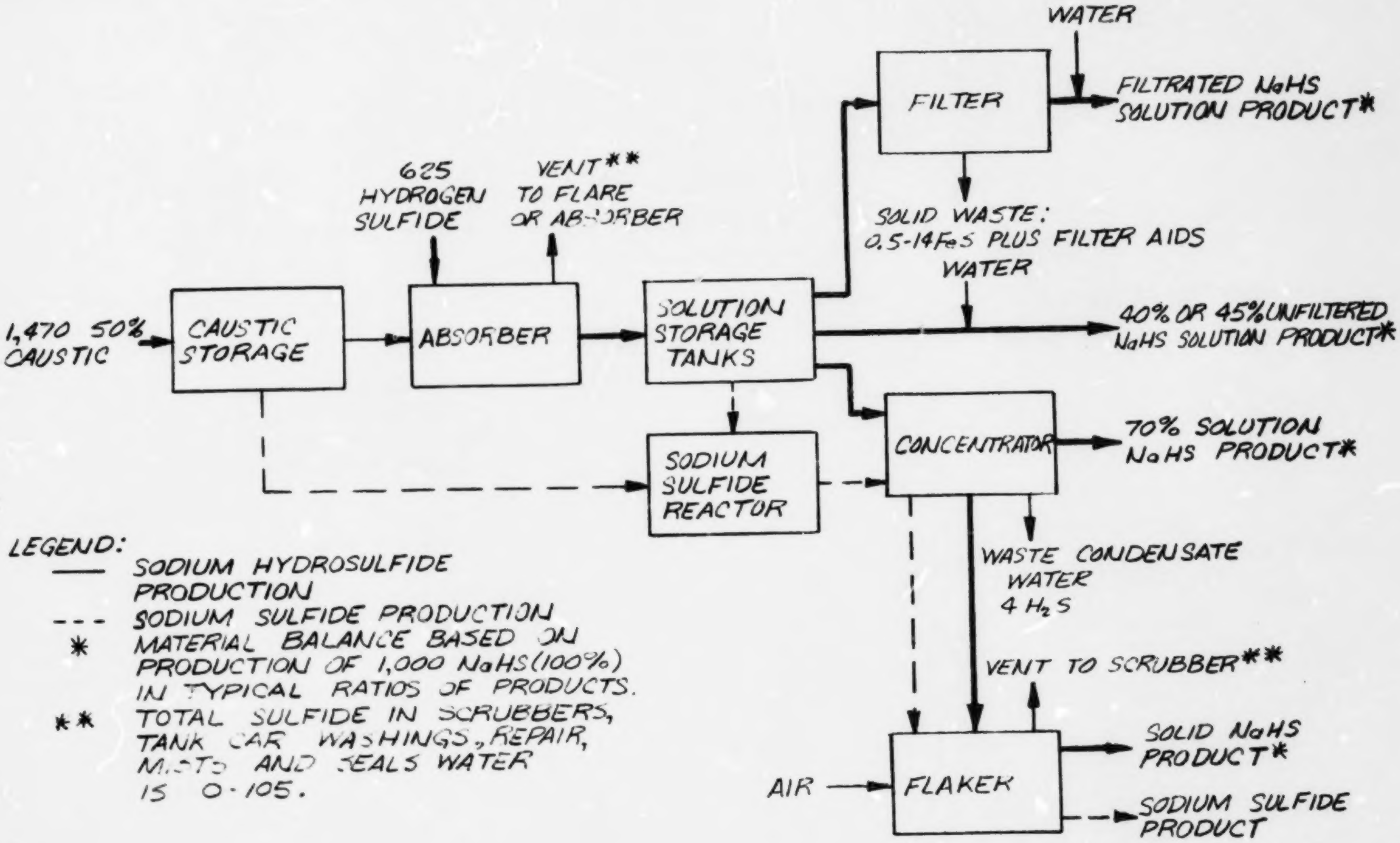

WATER
FILTER
FILTRATED NaHS SOLUTION PRODUCT*
625 HYDROGEN SULFIDE
VENT** TO FLARE OR ABSORBER
SOLID WASTE: 0.5-14FeS PLUS FILTER AIDS
WATER
1,470 50% CAUSTIC
CAUSTIC STORAGE
ABSORBER
SOLUTION STORAGE TANKS
40% OR 45% UNFILTERED NaHS SOLUTION PRODUCT*
CONCENTRATOR
70% SOLUTION NaHS PRODUCT*
SODIUM SULFIDE REACTOR
WASTE CONDENSATE WATER 4 H2S
VENT TO SCRUBBER**
AIR
FLAKER
SOLID NaHS PRODUCT*
SODIUM SULFIDE PRODUCT
LEGEND:
— SODIUM HYDROSULFIDE PRODUCTION
- - - SODIUM SULFIDE PRODUCTION
* MATERIAL BALANCE BASED ON PRODUCTION OF 1,000 NaHS(100%) IN TYPICAL RATIOS OF PRODUCTS.
** TOTAL SULFIDE IN SCRUBBERS, TANK CAR WASHINGS, REPAIR, MISTS AND SEALS WATER IS 0-105.

FIGURE 5-54

MANUFACTURE OF SODIUM HYDROSULFIDE AND SODIUM SULFIDE

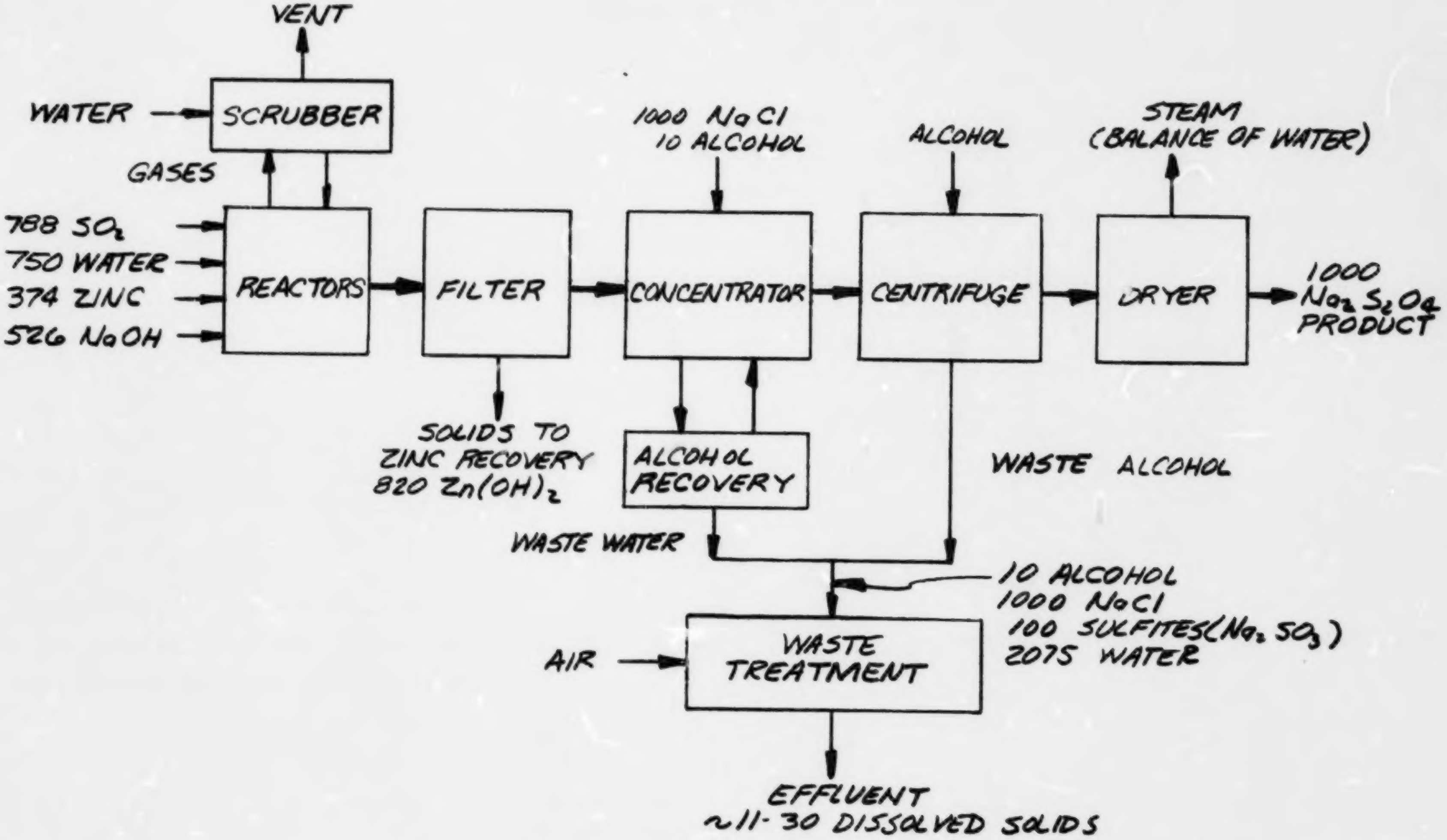


FIGURE 5-55

SODIUM HYDROSULFITE MANUFACTURE
BY ZINC PROCESS

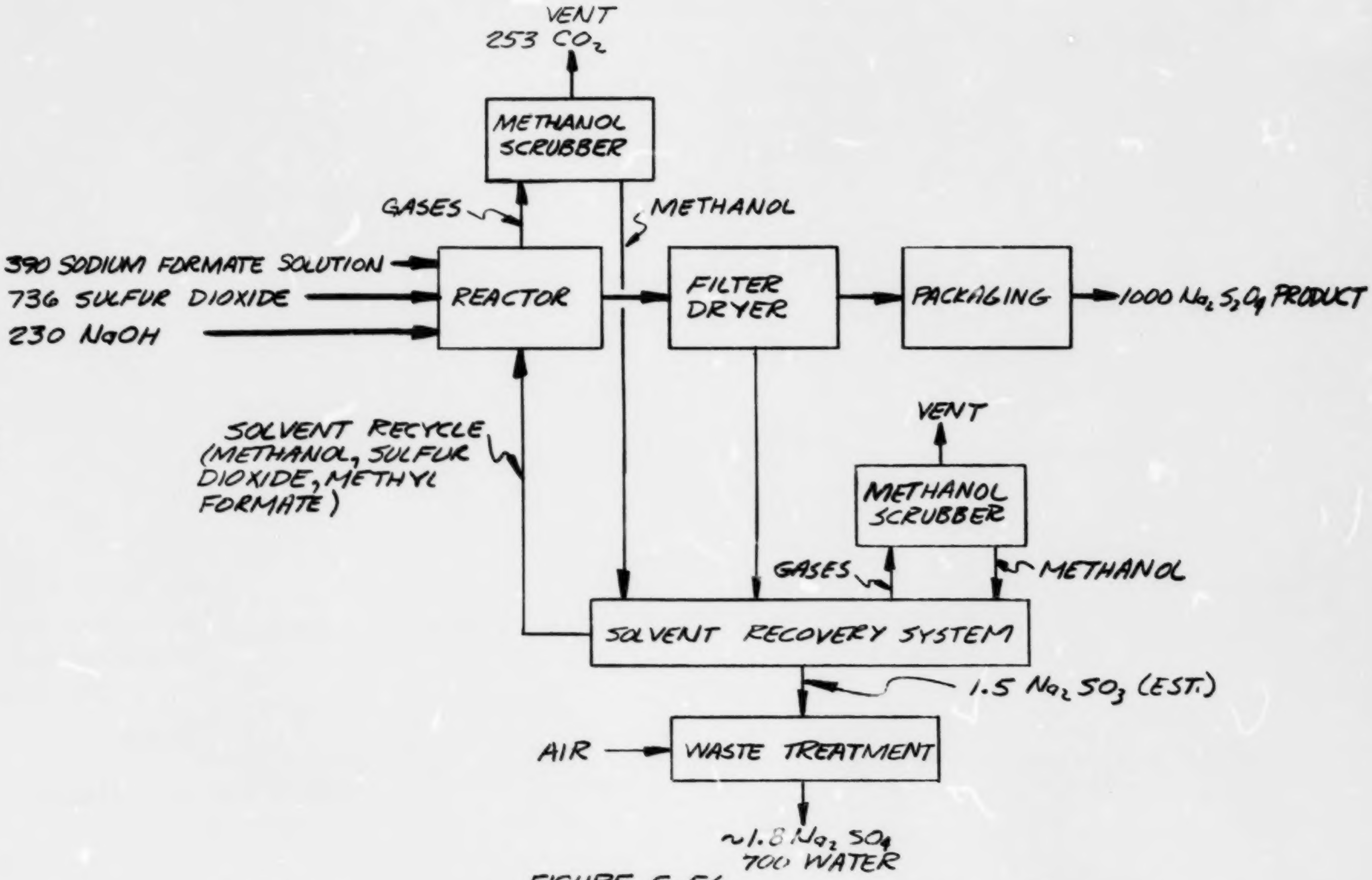


FIGURE 5-56
SODIUM HYDROSULFITE MANUFACTURE

resulting zinc hydrosulfite in solution is treated with caustic soda to precipitate zinc hydroxide. The sodium hydrosulfite solution is filtered and evaporated, and the hydrosulfite is crystallized out, centrifuged, washed, dried, and packaged for sale. Most of the wastes from this process are waterborne. The only solid waste generated is zinc oxide or zinc carbonate formed as a co-product during the conversion of the zinc hydrosulfite intermediate to the sodium salt. The zinc oxide or carbonate is recovered and sold as a coproduct. No hazardous wastes are destined for land disposal, and no solid wastes are generated that are not sold or recycled.

In the second process, sodium hydrosulfite is also produced by a reaction of SO_2 with sodium formate in an alcohol based solvent. All of the wastes from this process are waterborne and no hazardous wastes are generated.

5.5.5.9 Sodium Metal

This material is made by the Down's Cell process and is a co-product of chlorine, SIC Code 28121.

5.5.5.10 Sodium Silicofluoride

This product is made by two processes as shown in Figures 5-57 and 5-58. In the first, fluosilicic acid, H_2SiF_6, is reacted in solution with sodium chloride. The product is then separated by filtration, dried, and packaged. All of the wastes from this process are water-borne, and treatment of this effluent does generate a small amount of some calcium fluoride containing wastes. This treatment consists in general of precipitation with lime and settling or filtering of solids.

In the second process, soda ash is added to impure phosphoric acid. Sodium silicofluoride precipitates and is collected by filtration, washed, dried, and packaged. Wastes from this process are all water-borne, and their treatment generates a solid waste-containing calcium fluoride by a treatment process as described above. This second process is used in only one facility, and the amount of waste material is small.

For both processes, the concentration of CaF_2 in the solid waste is such that the overall biological properties of the waste are similar to those described in Appendix A for CaF_2. Protection against contamination of ground and surface waters is required. See Section 5.5.2.5 for a detailed discussion of the potentially hazardous nature of such wastes.

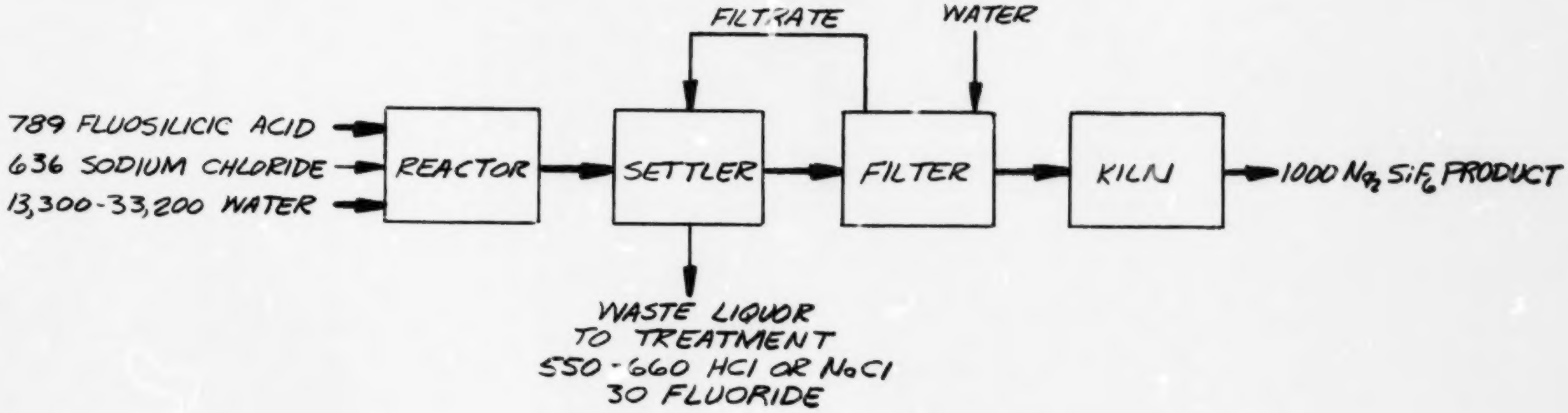


FIGURE 5-57

SODIUM SILICOFLUORIDE MANUFACTURE

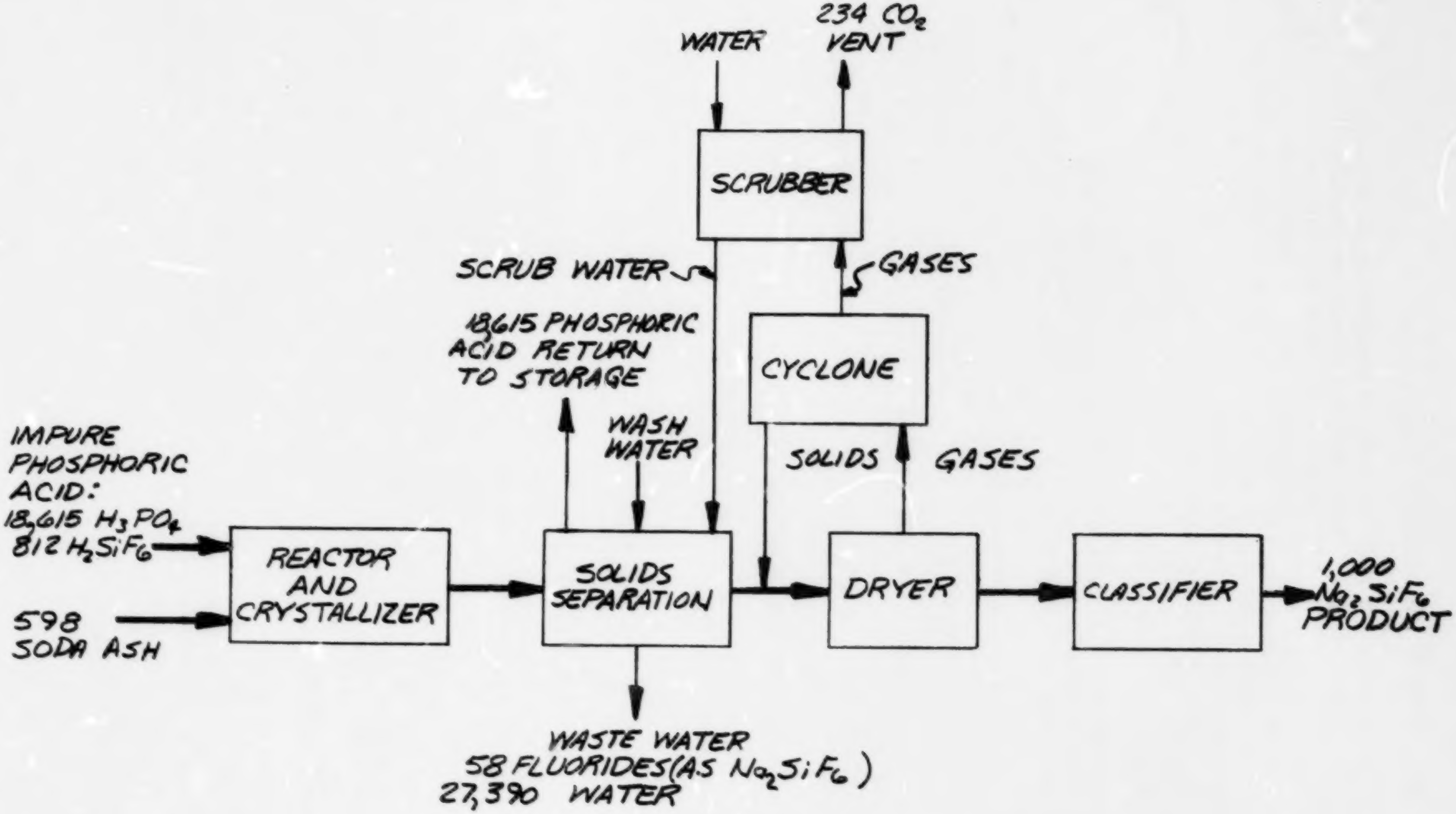


FIGURE 5-58

SODIUM SILICOFLUORIDE MANUFACTURE FROM AN IMPURE PHOSPHORIC ACID STREAM

5.5.5.11 Sodium Phosphates

The manufacture of sodium orthophosphates (monobasic, dibasic, and tribasic sodiumphosphates) is shown in Figure 5-59. These materials are made by the reaction of phosphoric acid with soda ash or caustic soda. No hazardous wastes are generated, the only significant wastes being leaks and spills of reactants or products. Sodium tripolyphosphate is manufactured (as is shown in Figure 5-60) from the orthophosphate solution by molecular dehydration with heat. No hazardous wastes are generated by this process.

Food-grade sodium phosphate is prepared from high purity, food-grade phosphoric acid. The only wastes are dilute solutions of phosphoric acid due to equipment washdown, scrubbers, spills and the like that are not recycled due to the food-grade requirements. These wastes are not hazardous; several widely sold soft drinks are also dilute solutions of phosphoric acid. The facilities responsible for production of food-grade phosphoric acid from phosphorus are covered under a different classification, SIC 2874 (see pp. 124,609 and 610 reference 71) and hence any wastes associated with those operations are not attributable to the industries of this study (SIC 281).

5.5.5.12 Sodium Borohydride

The manufacture of sodium borohydride is shown in Figure 5-61. Sodium metal and hydrogen are reacted in an oil medium to yield the hydride. The oil solution of this material is then reacted with methyl borate to yield sodium borohydride, which is separated from the oil into a aqueous phase and recovered by evaporation. The oil is recycled.

Most of the wastes from this process (sodium borate and methane) are not hazardous. The only hazardous waste consists of unreacted sodium sludge in the first process step. This sludge is not a candidate for land disposal because of the potential for explosion upon contact with water. It is currently (and for the foreseeable future) disposed of by barging to sea. The amounts so disposed presently are estimated to be 20 metric tons per year from Massachusetts and 10 metric tons per year from Pennsylvania.

5.5.5.13 Sodium Sulfite

As shown in Figure 5-62, sodium sulfite is produced by reaction of SO_2 in solution with soda ash under pressure. Small amounts of iron sulfide solid waste are produced from waste water treatment. This material is extremely insoluble

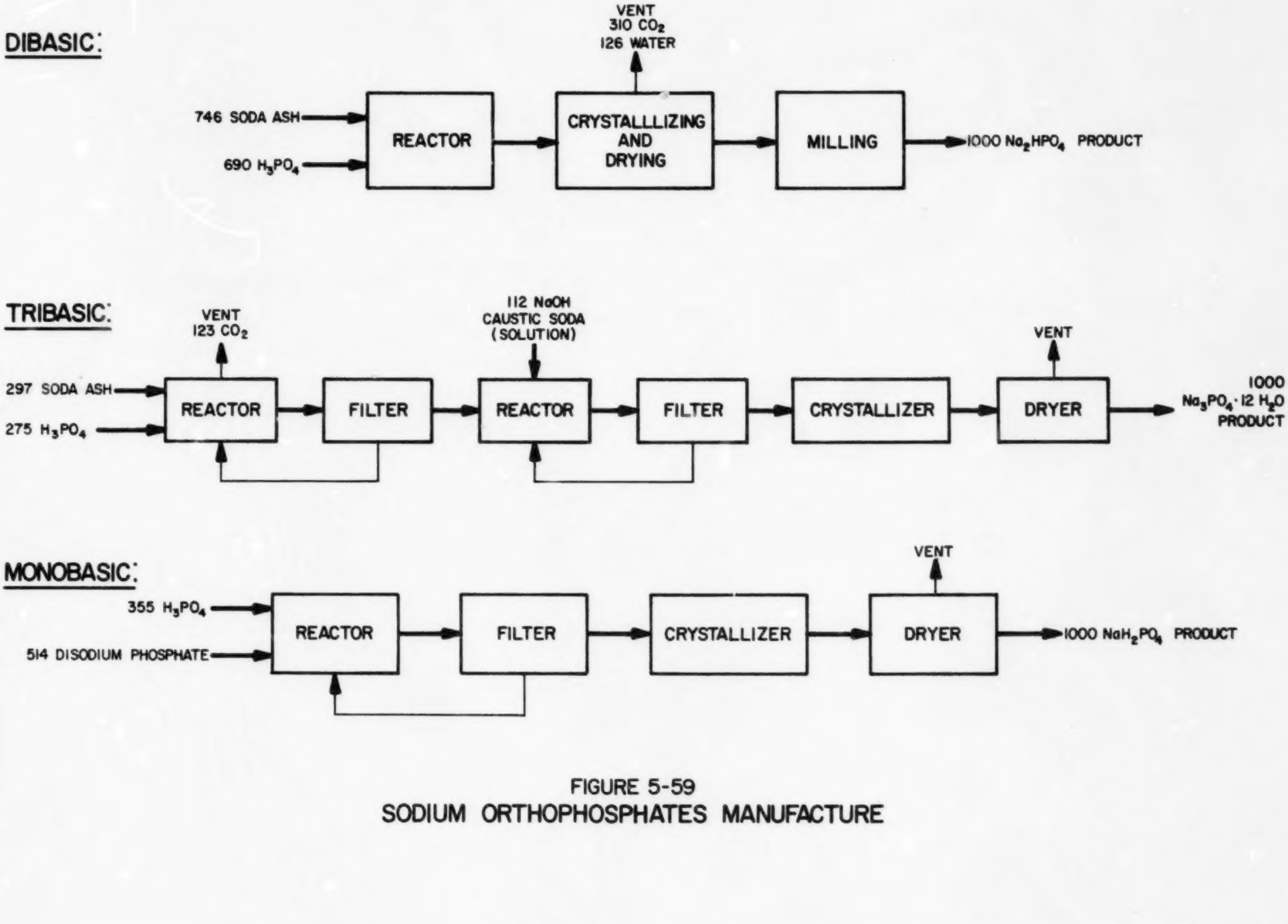


FIGURE 5-59
SODIUM ORTHOPHOSPHATES MANUFACTURE

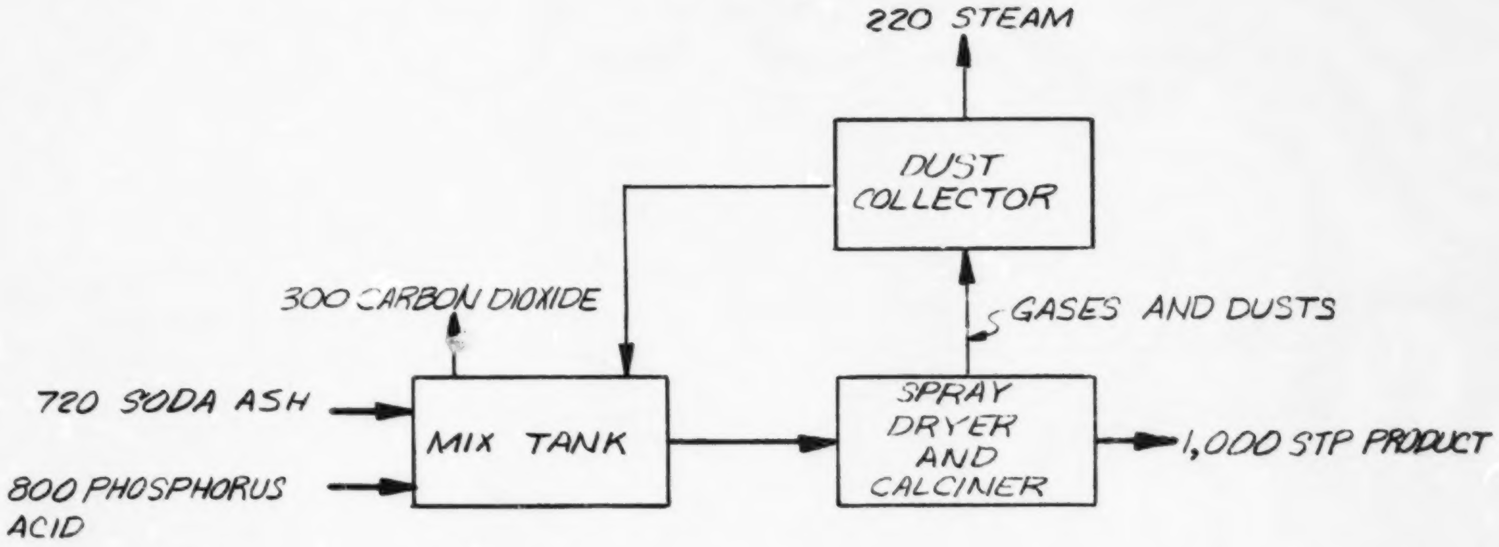


FIGURE 5-60
SODIUM TRIPOLYPHOSPHATE MANUFACTURE

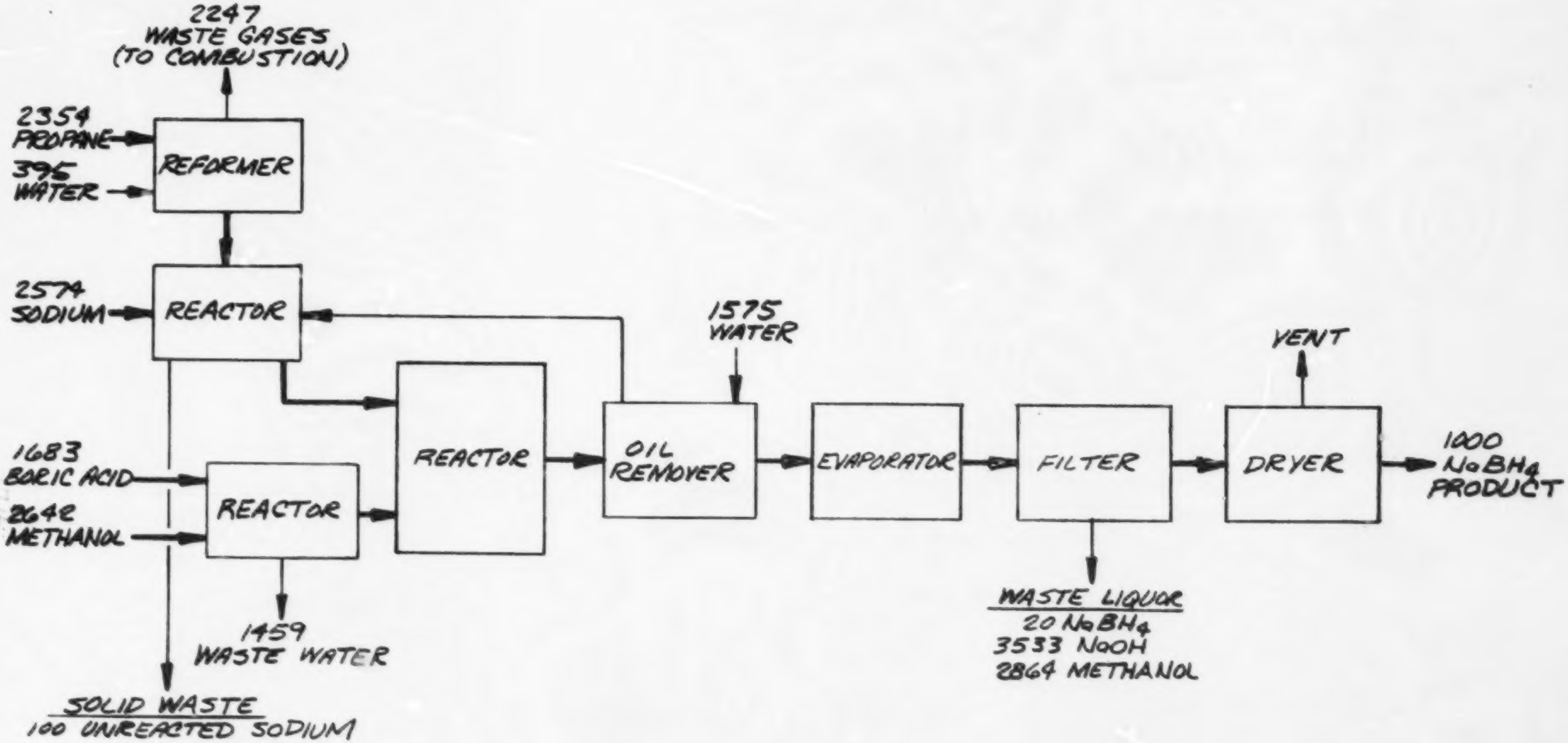


FIGURE 5-61

SODIUM BOROHYDRIDE MANUFACTURE

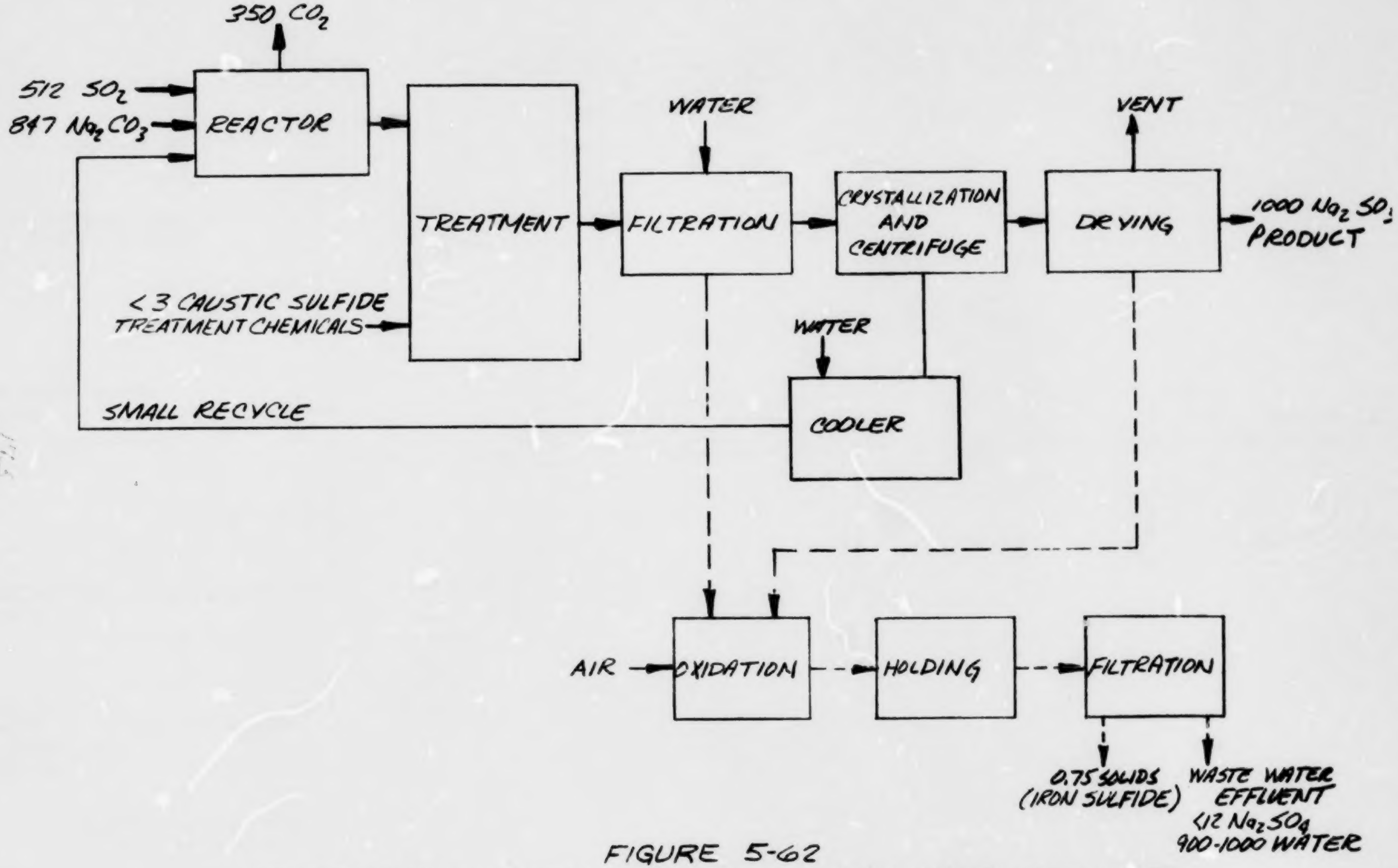


FIGURE 5-62
SODIUM SULFITE MANUFACTURE

in water, and dilute acid and is not hazardous. The properties of iron sulfide are given in Appendix A.

5.5.5.14 Sodium Silicate

As shown in Figure 5-63, sodium silicate is produced by reaction of silica sand with caustic soda. These mixed in the desired proportion and charged to a furnace. Water and steam are added to the product under pressure to completely dissolve the silicate. The liquid product is then stored or used to produce silicate in solid form. The production of solid silicate from silicate solution essentially involves evaporation of the water, although the silicate in solution may be further reacted with a caustic solution during the process if a higher sodium crude content is desired in the solid product. This is typically the case in the production of sodium metasilicate (anhydrous) from tetrasilicate water glass. The dried anhydrous silicate is screened and milled to achieve the desired particle sizes. The only solid wastes generated are due to treatment of water-borne waste streams and consist of silica and silicates. These are not hazardous.

5.5.5.15 Sodium Thiosulfate

As shown in Figure 5-64, this material is made by reaction of sodium sulfite with sulfur. The feed solution to the reaction may also contain sodium bisulfite and sodium carbonate. The resulting hypo solution may be sold at 30 percent solids or may be further processed to yield anhydrous solid hypo or the pentahydrate. The hydrate is crystallized out during vacuum evaporation, and is washed, dried and packaged. In the manufacture of the anhydrous material, the hydrate is melted, treated with caustic soda, sodium hydrodulfide, and copper chloride, then filtered. Anhydrous crystals are formed in a high-temperature crystalliaer, centrifuged, dried, and packaged. Generally there are no process wastes; leaks and spills are waterborne and not hazardous.

5.5.5.16 Chlorates and Perchlorates

The manufacture of sodium and potassium chlorate is shown in Figures 5-65 and 5-66. Sodium or potassium chloride is dissolved in water and impurities are removed by the addition of soda ash and caustic. Calcium carbonate and magnesium hydroxide precipitate out and are removed by filtration and discarded as non-hazardous wastes. The brine is acidified and dichromate is added and it is electrolyzed. Chlorates and hydrogen gas are the products.

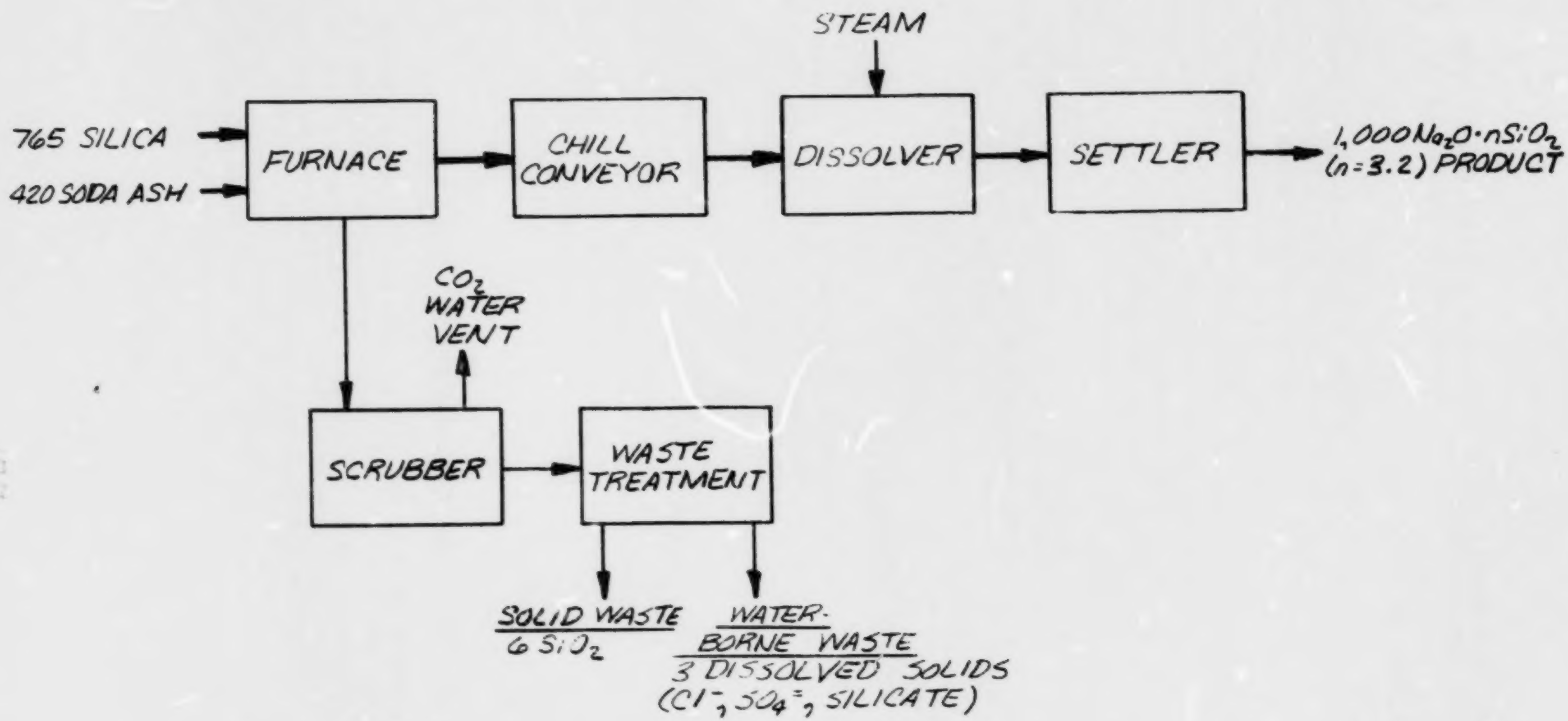


FIGURE 5-63
SODIUM SILICATE MANUFACTURE

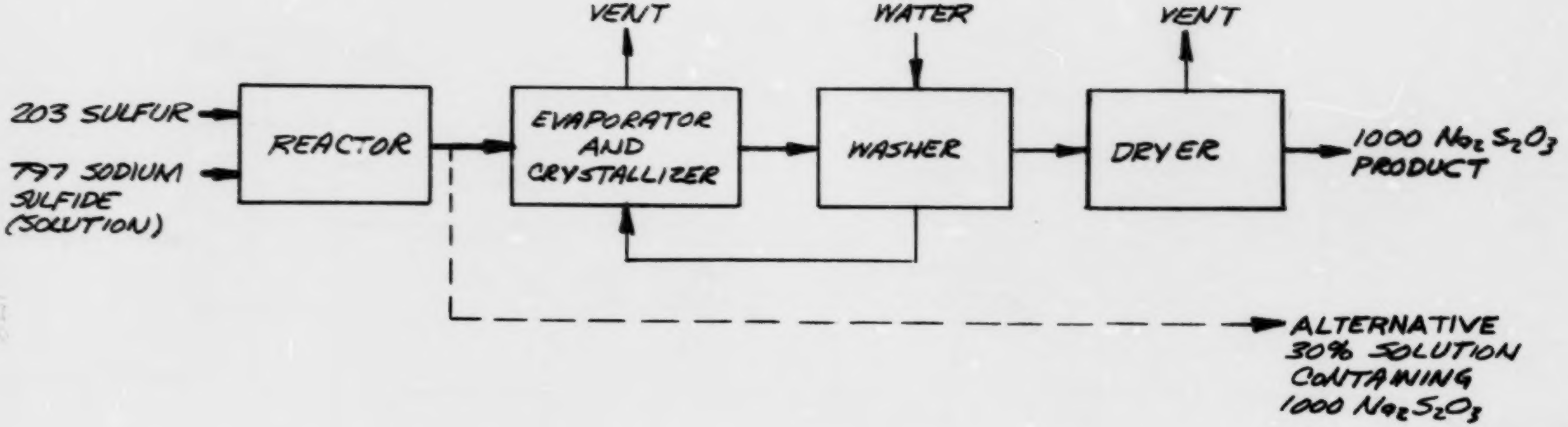
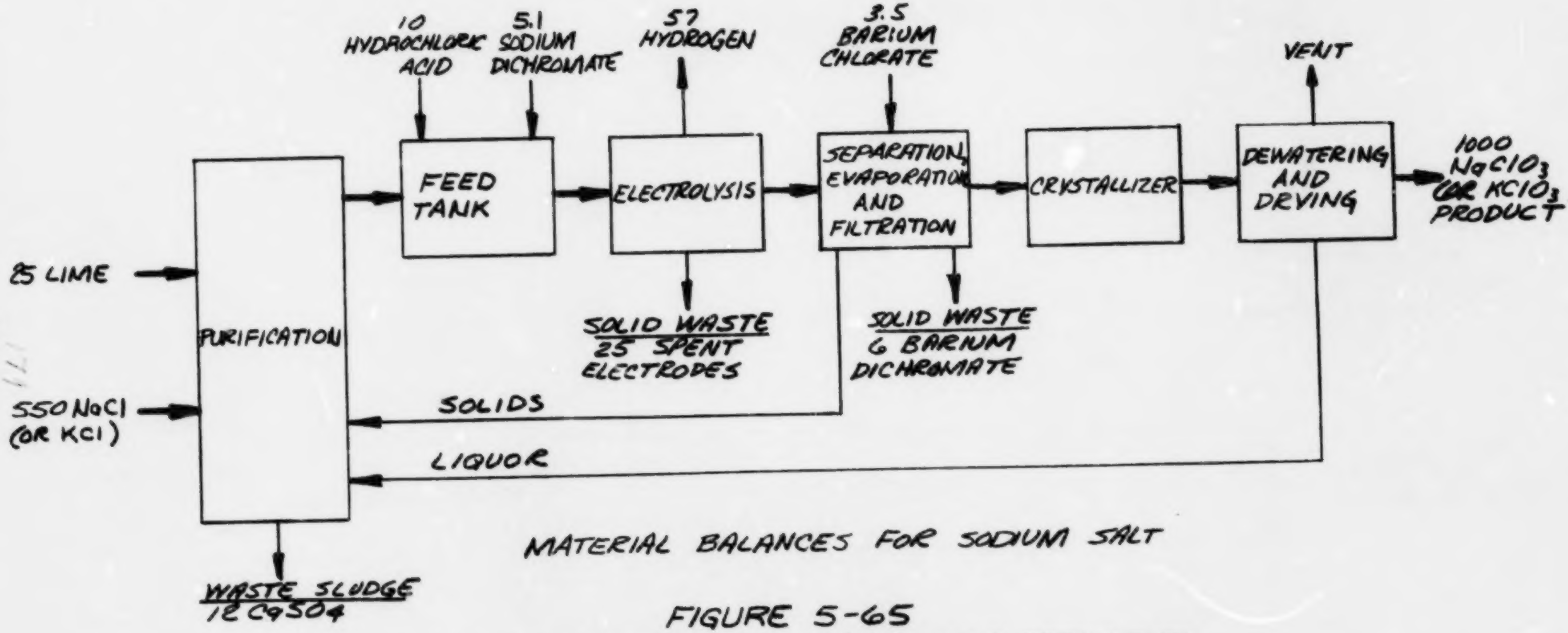

VENT
WATER
VENT
203 SULFUR
797 SODIUM SULFIDE (SOLUTION)
REACTOR
EVAPORATOR AND CRYSTALLIZER
WASHER
DRYER
1000 $Na_2S_2O_3$ PRODUCT
ALTERNATIVE 30% SOLUTION CONTAINING 1000 $Na_2S_2O_3$

FIGURE 5-64

SODIUM THIOSULFATE MANUFACTURE



MATERIAL BALANCES FOR SODIUM SALT

FIGURE 5-65
CHLORATES MANUFACTURE

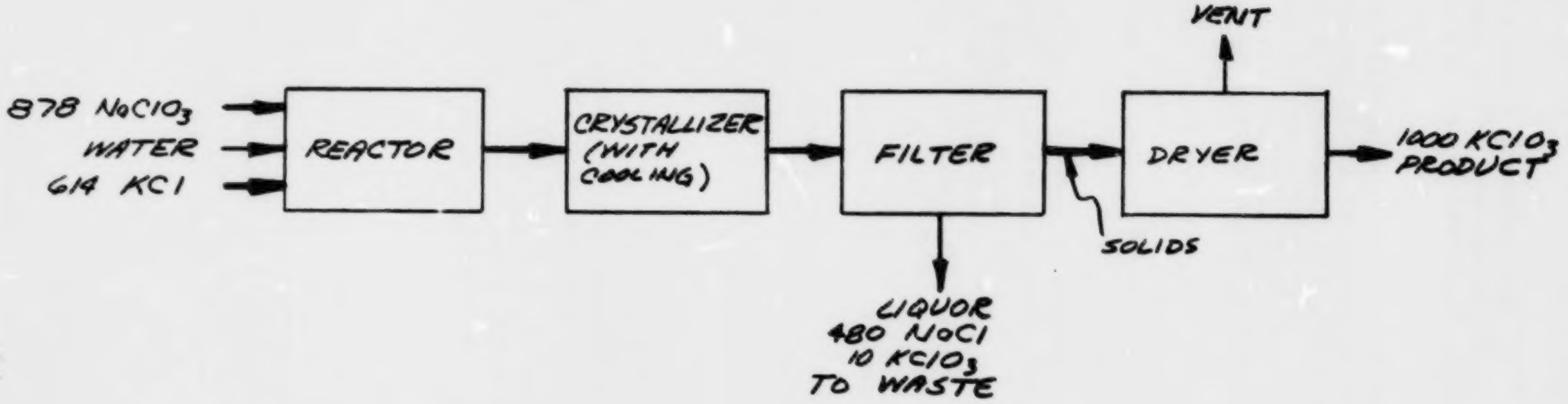


FIGURE 5-66
POTASSIUM CHLORATE MANUFACTURE
ALTERNATE PROCESS

Barium chloride is added to the solution coming from the cell to remove sulfates and chromates. This small amount of material is then removed by filtration and discarded as a solid waste.

The constituents in this waste are barium sulfate which is non-hazardous and barium chromate which is hazardous. The properties of barium chromate are discussed in Appendix A. The solutions are then partialy evaporated to recover unreacted chlorides which are recycled and then fed to crystallizers to recover the product ($KClO_3$ or $NaClO_3$).

There is also an additional solid waste consisting of spent carbon electrodes contaminated with chlorates. These are probably combustible and must be disposed of with care, but are not otherwise hazardous.

As shown in Figure 5-67, sodium perchlorate is prepared by further electrolysis of chlorate solutions. Hydrogen is again formed as a co-product, and small amounts of barium chromate hazardous waste is generated and goes to disposal on land, insofar as is known. The amounts in any one location would be very small, less than one metric ton per year, and hence are not considered further. These would be expected to be found principally in Nevada.

Potassium perchlorate is produced by reaction of KCl with the sodium salt in solution as shown in Figure 5-68. As $KClO_4$ is very sparingly soluble, it is recovered by filtration. No hazardous wastes are produced or destined for disposal on land.

5.5.5.17 Potassium Nitrate

This material is manufactured by two processes, as shown in Figure 5-69. Only one process, the reaction of potassium chloride with sodium nitrate, has any significant wastes, and these are salt (sodium chloride) solutions which are not hazardous in these amounts at these locations. The other process, combining potassium chloride with nitric acid in air, generates no wastes.

5.5.5.18 Sodium Bisulfite

This commodity is produced from sulfur dioxide and soda ash by reaction in aqueous solution. The raw materials are of high purity and introduce no hazardous wastes by virtue of impurities. Sodium bisulfite manufacture has only a water-borne discharge of dilute sodium sulfate. No hazardous wastes are generated. The flow diagram is given in Figure 5-70.

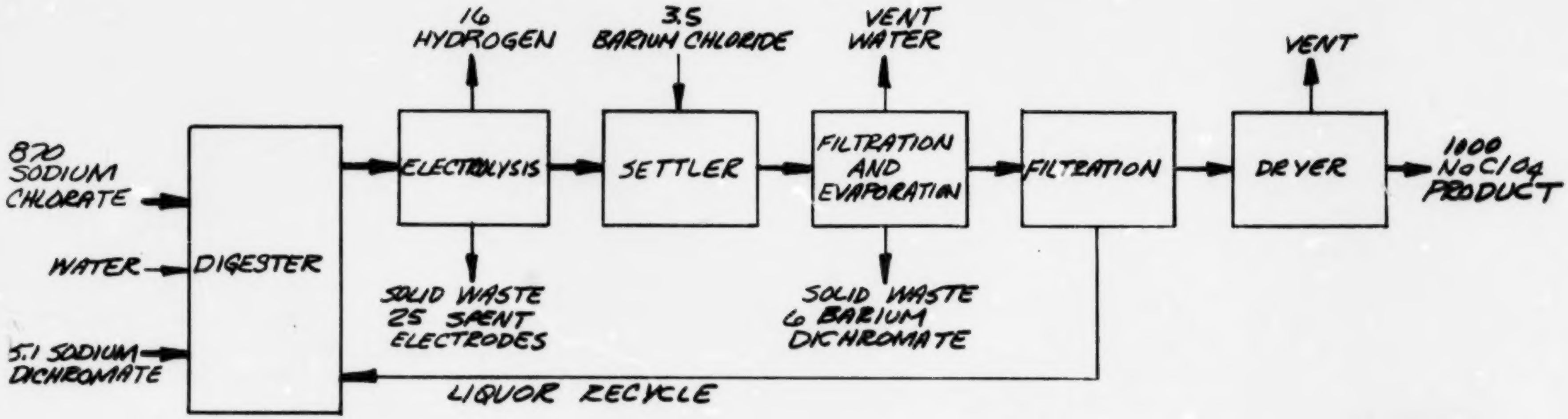


FIGURE 5-67
SODIUM PERCHLORATE MANUFACTURE

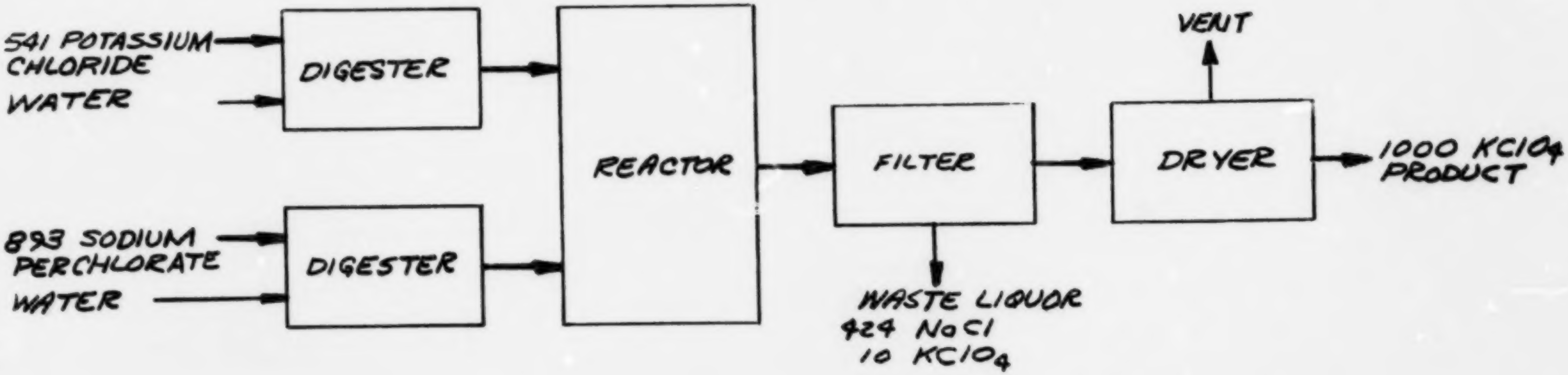
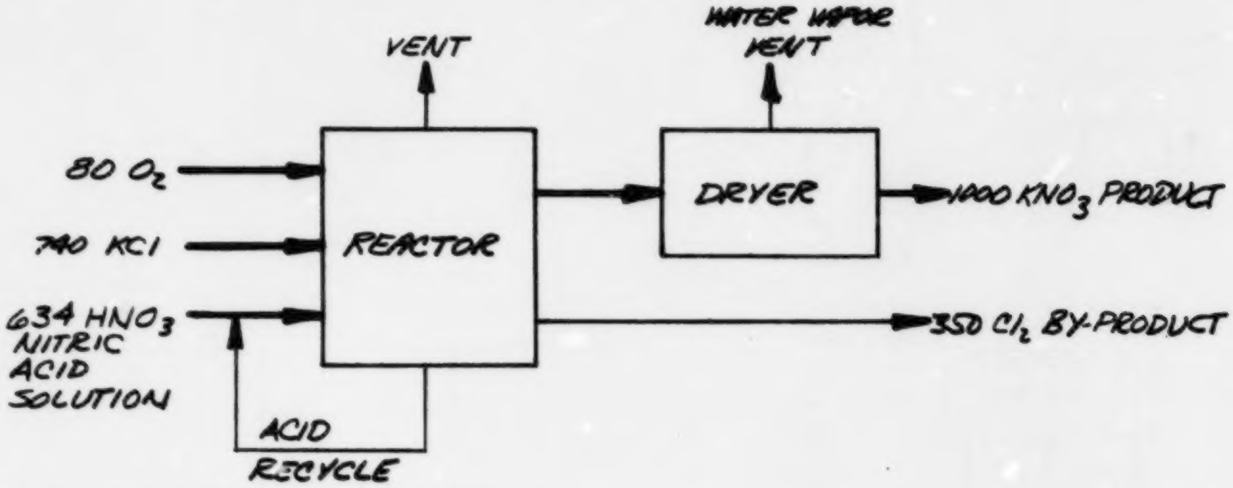


FIGURE 5-68
POTASSIUM PERCHLORATE MANUFACTURE



NITRIC ACID PROCESS

FROM SODIUM NITRATE

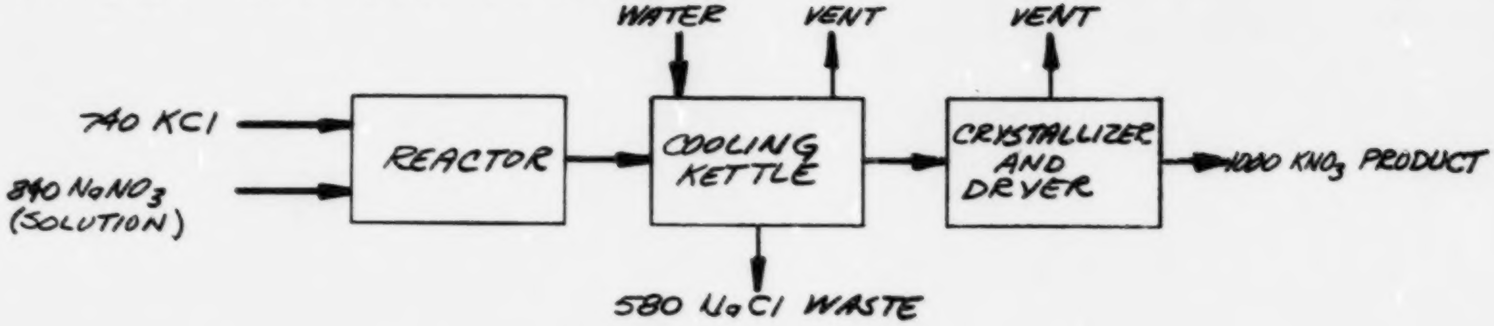


FIGURE 5-69
POTASSIUM NITRATE MANUFACTURE

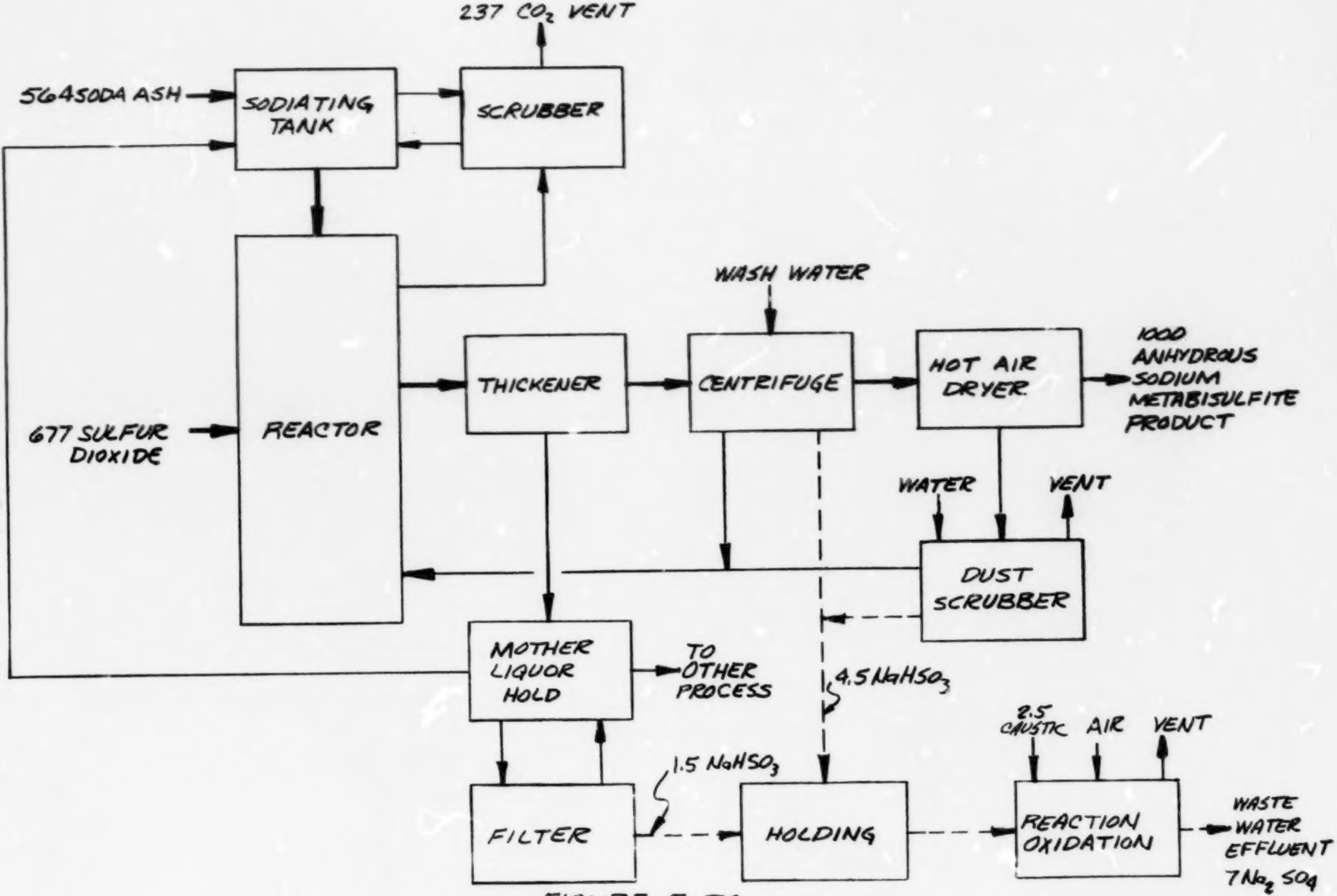


FIGURE 5-70
SODIUM BISULFITE MANUFACTURE

5.5.5.19 Sodium Bromide

Sodium bromide is produced from hydrobromic acid and soda ash or caustic soda in aqueous solution as shown in Figure 5-71. No significant wastes are generated.

5.5.5.20 Sodium Cyanide

This commodity is produced from hydrocyanic acid solution and caustic soda. Although sodium cyanide is itself a hazardous material, the manufacture of it is carried out very carefully using stoichiometric amounts of reactants and no wastes are generated from the process. The flow diagram is given in Figure 5-72.

5.5.5.21 Aggregate of SIC 28197 Hazardous Wastes to Land Disposal

The processes in SIC 28197 generating significant amounts of hazardous wastes for land disposal are the manufacture of sodium silicofluoride and borax. However, the wastes from borax manufacture are not further considered because of the special conditions discussed earlier with regard to the singular location in an arid region that poses no environmental difficulty under present or future operation.

The aggregate of the fluoride-containing hazardous waste streams of SIC 28197 are given in Table 5-11 on a state-by-state, regional and national basis. The values are based on both manufacturer-supplied data and estimates, and are reliable to within 30 percent of the given values.

5.5.5.22 Projection of SIC 28197 Hazardous Wastes Destined for Land Disposal

The projections given in Table 5-11 take into account the growth of these industries (estimated as 4 percent per year over the period) and the impact of air and water regulations (which is minor) on the total amounts. No process changes are anticipated that would significantly affect the land-destined hazardous waste generation.

The trend of hazardous waste destined for land disposal in SIC 28197 can be summarized in terms of metric tons per year (short tons per year) as:

186

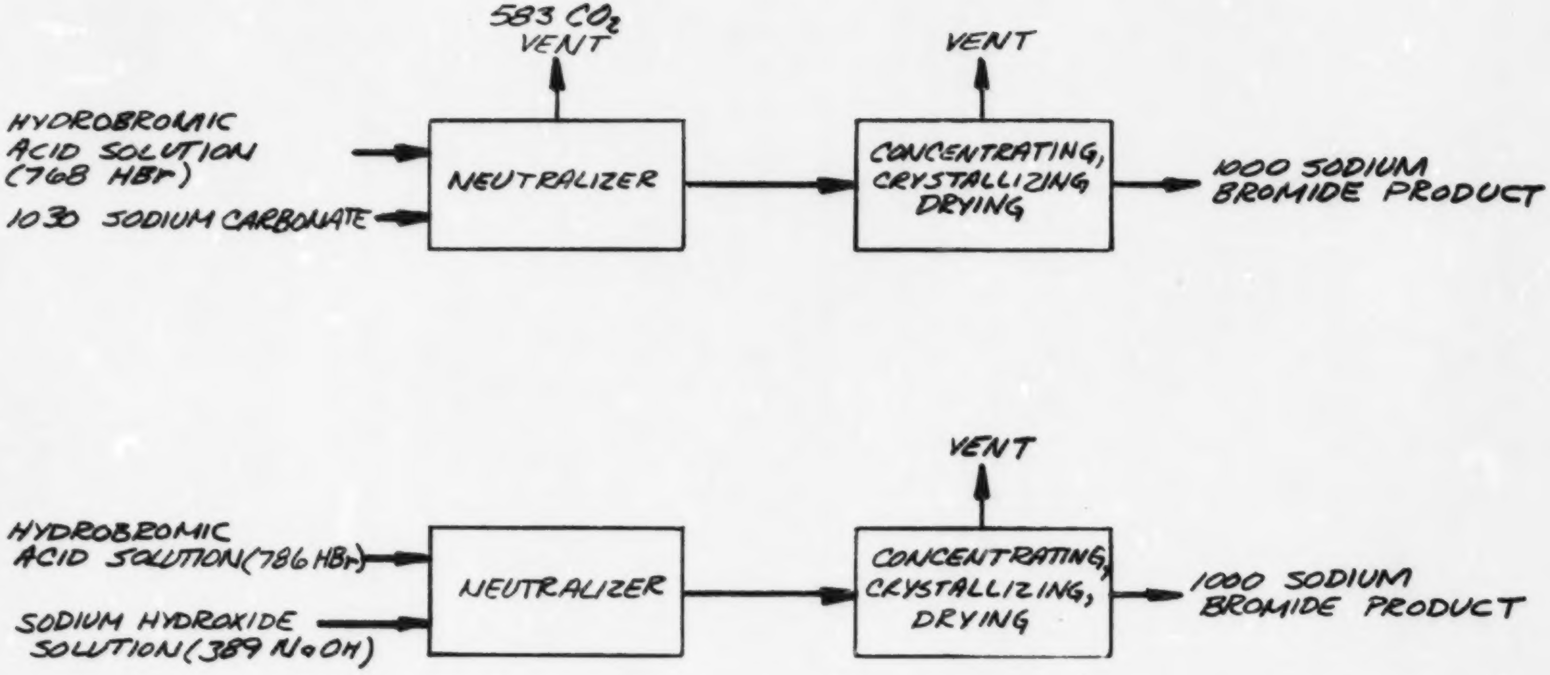

HYDROBROMIC ACID SOLUTION (768 HBr)
1030 SODIUM CARBONATE
583 CO_2 VENT
NEUTRALIZER
VENT
CONCENTRATING, CRYSTALLIZING DRYING
1000 SODIUM BROMIDE PRODUCT
HYDROBROMIC ACID SOLUTION (786 HBr)
SODIUM HYDROXIDE SOLUTION (389 NaOH)
NEUTRALIZER
VENT
CONCENTRATING, CRYSTALLIZING, DRYING
1000 SODIUM BROMIDE PRODUCT

FIGURE 5-71
SODIUM BROMIDE MANUFACTURE

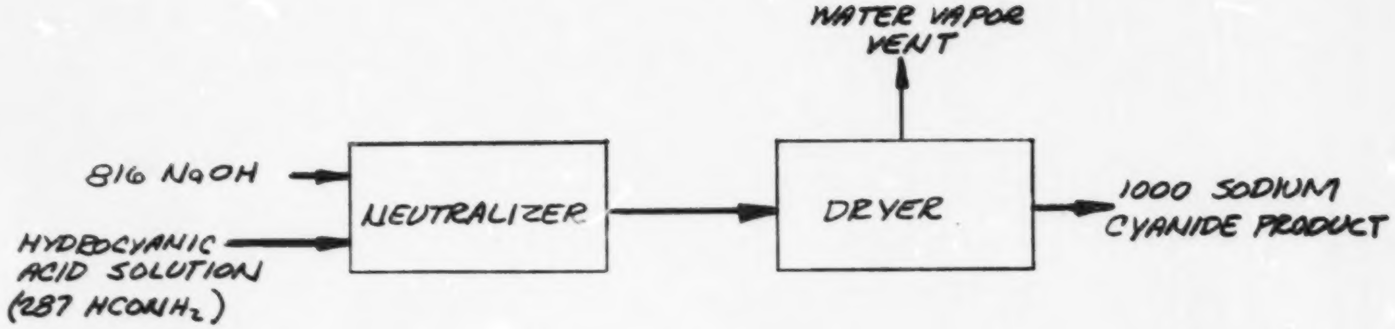

816 NaOH
HYDROCYANIC ACID SOLUTION ($287\ HCONH_2$)
NEUTRALIZER
DRYER
WATER VAPOR VENT
1000 SODIUM CYANIDE PRODUCT

FIGURE 5-72
SODIUM CYANIDE MANUFACTURE

Table 5-11. Hazardous Wastes Destined for Land Disposal from the SIC 28197 Potassium and Sodium Compounds Manufacture (metric tons per year, dry basis)

		Current		1977		1983	
		Total Hazardous Wastes	Fluoride Content	Total Hazardous Wastes	Fluoride Content	Total Hazardous Wastes	Fluoride Content
IV	Alabama						
X	Alaska						
IX	Arizona						
VI	Arkansas						
IX	California						
VIII	Colorado						
I	Connecticut						
III	Delaware						
IV	Florida	2,900	1,400	3,300	1,600	3,700	1,800
IV	Georgia	200	100	300	100	400	200
IX	Hawaii						
X	Idaho						
V	Illinois	600	300	600	340	700	380
V	Indiana						
VII	Iowa						
VII	Kansas						
IV	Kentucky						
VI	Louisiana						
I	Maine						
III	Maryland						
I	Massachusetts						
V	Michigan						
V	Minnesota						
IV	Mississippi						
VII	Missouri						
VIII	Montana						
VII	Nebraska						
IX	Nevada						
I	New Hampshire						
II	New Jersey	200	100	300	100	400	200
VI	New Mexico						
II	New York						
IV	North Carolina						
VIII	North Dakota						
V	Ohio						
VI	Oklahoma						
X	Oregon						
III	Pennsylvania						
I	Rhode Island						
IV	South Carolina						
VIII	South Dakota						
IV	Tennessee						
VI	Texas	500	270	600	300	800	370
VIII	Utah						
I	Vermont						
III	Virginia						
X	Washington						
III	West Virginia						
V	Wisconsin						
VIII	Wyoming						
TOTAL		4,400	2,200	5,100	2,400	6,000	3,000
Region I							
II		200	100	300	100	400	200
III							
IV		3,100	1,500	3,600	1,700	4,100	2,000
V		600	300	600	340	700	380
VI		500	270	600	300	800	370
VII							
VIII							
IX							
X							

Period	Current	1977	1983
dry basis	4,400 (4,800)	5,100 (5,600)	6,000 (6,600)
moisture included	280,000 (310,000)	320,000 (350,000)	300,000 (420,000)

The large estimated water content of these wastes is due to the use of deep-welling (at one plant) which requires a very dilute slurry for pumping.

5.5.6 Catalysts (SIC 28198)

There are a large number of materials falling into this category. Generally, most of the industrial catalysts are prepared in one of two ways:

(a) the support material (silica, alumina, carbon, silica alumina or zeolite) is first impregnated with a solution of the desired metal or metals salts (Pt, Pd, Rh, Ni, Co, Mo, Cu, V). If the salt used is thermally unstable, this material is then merely calcined in air to yield a supported oxide catalyst.

(b) if the impregnating salt is thermally stable, a second impregnation with either aqueous ammonia or caustic soda effects formation of a supported hydroxide which is then washed and calcined. This material is then generally packaged and shipped as is to the user. If the user desires the metal and not the oxide, hydrogen reduction is normally carried out at the user's facility.

The exception to the above rule is with the noble metal systems (Pt, Pd, Rh). These are generally reduced with hydrogen at the manufacturers plant. In these cases, also, the impregnating salt is generally not first converted to the oxide, but, rather, is directly reduced to the metal.

Contacts with a number of manufacturers of these materials have revealed that most of the off-batches and spilled materials are collected and sold for scrap value. Only small amounts of oxide materials arising from spillages are wastes, and these are generally insoluble and nonhazardous.

Flow diagrams for supported metal and metal oxide catalysts are given in Figures 5-73 and 5-74.

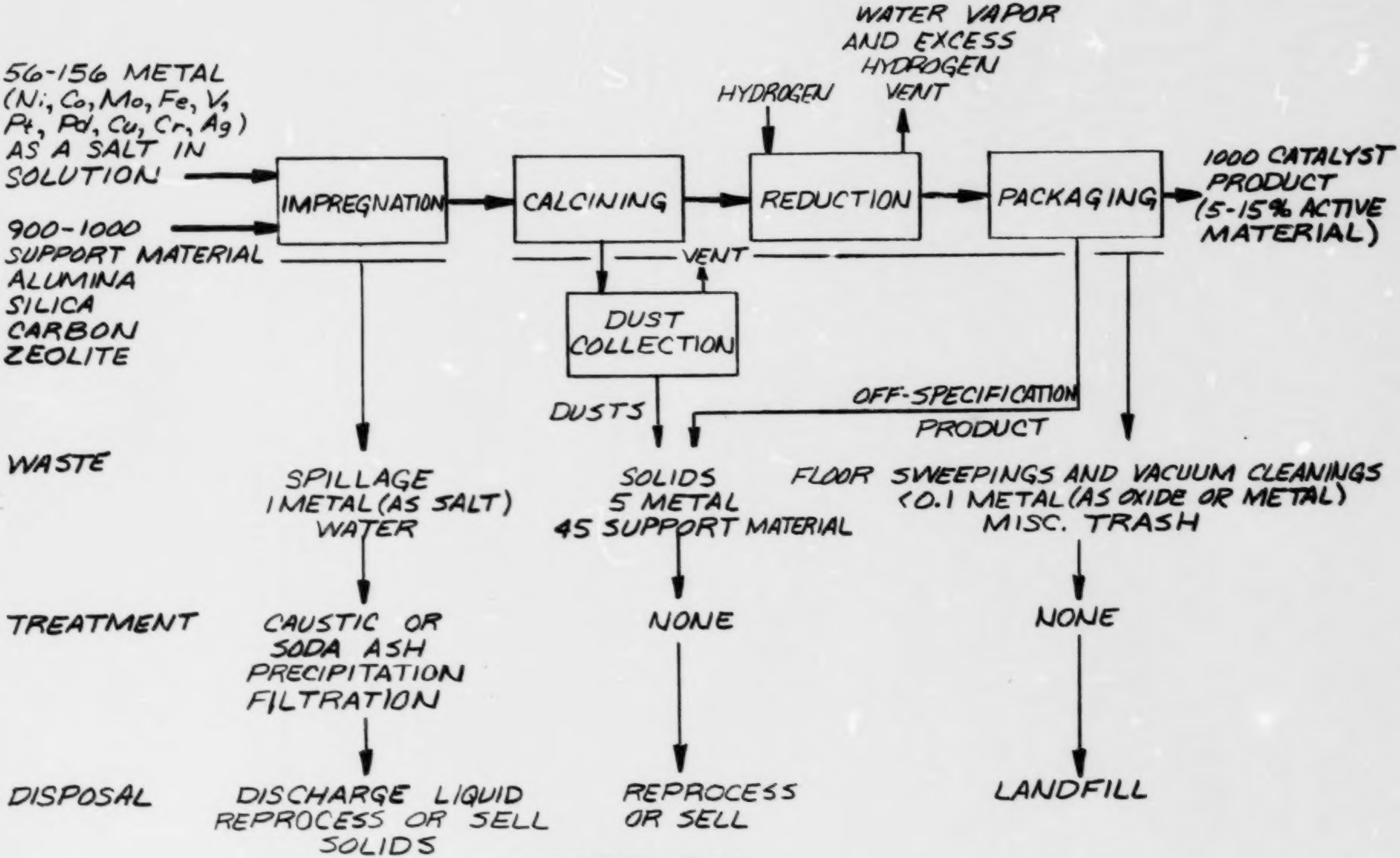

56-156 METAL
(Ni, Co, Mo, Fe, V, Pt, Pd, Cu, Cr, Ag)
AS A SALT IN SOLUTION
900-1000 SUPPORT MATERIAL
ALUMINA
SILICA
CARBON
ZEOLITE
IMPREGNATION
CALCINING
HYDROGEN
WATER VAPOR AND EXCESS HYDROGEN VENT
REDUCTION
PACKAGING
1000 CATALYST PRODUCT (5-15% ACTIVE MATERIAL)
VENT
DUST COLLECTION
DUSTS
OFF-SPECIFICATION PRODUCT
WASTE
SPILLAGE
1 METAL (AS SALT)
WATER
SOLIDS
5 METAL
45 SUPPORT MATERIAL
FLOOR SWEEPINGS AND VACUUM CLEANINGS
<0.1 METAL (AS OXIDE OR METAL)
MISC. TRASH
TREATMENT
CAUSTIC OR SODA ASH PRECIPITATION FILTRATION
NONE
NONE
DISPOSAL
DISCHARGE LIQUID REPROCESS OR SELL SOLIDS
REPROCESS OR SELL
LANDFILL

FIGURE 5-73
MANUFACTURE OF SUPPORTED METAL CATALYST MATERIALS

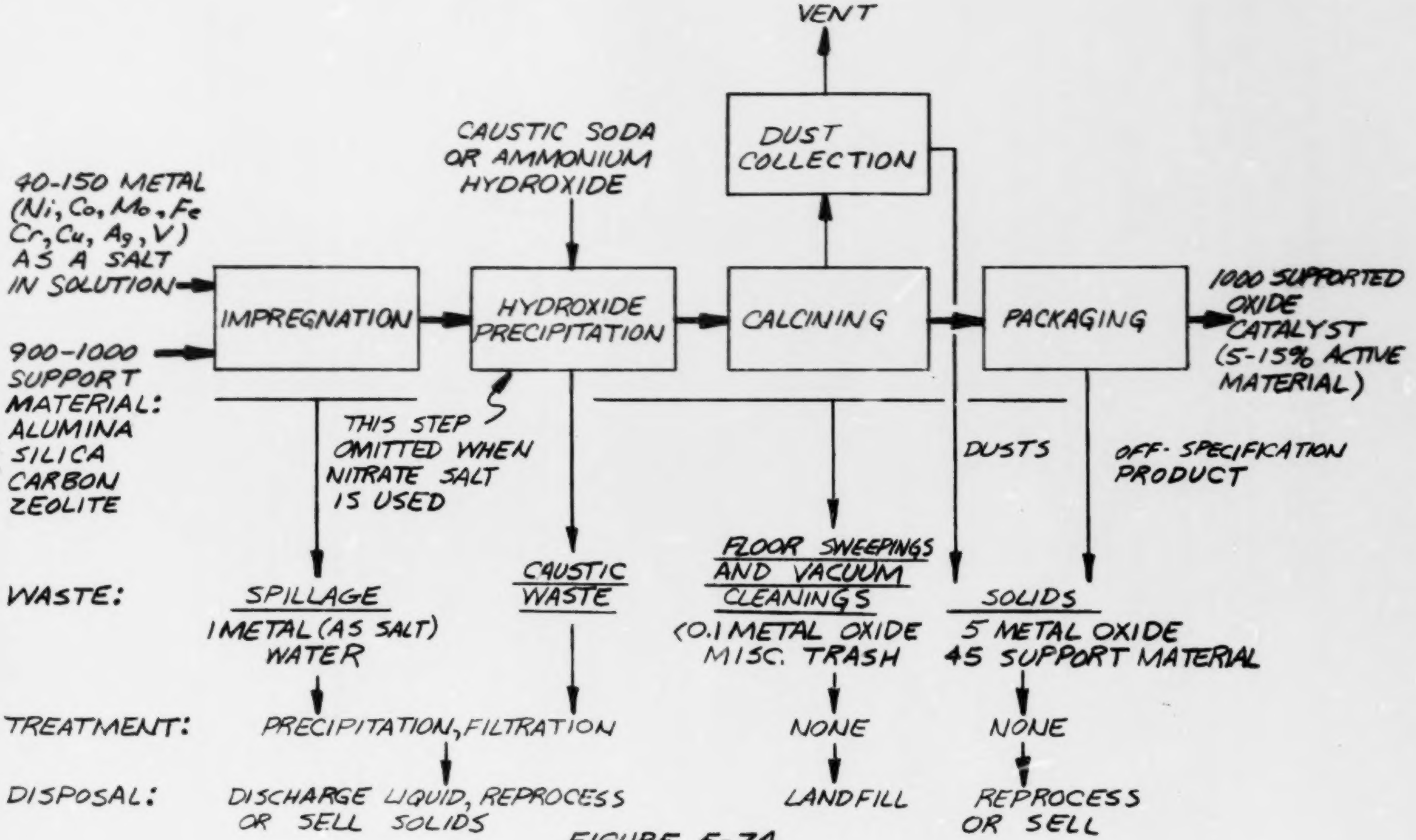

VENT
DUST COLLECTION
CAUSTIC SODA OR AMMONIUM HYDROXIDE
40-150 METAL (Ni, Co, Mo, Fe Cr, Cu, Ag, V) AS A SALT IN SOLUTION
900-1000 SUPPORT MATERIAL: ALUMINA SILICA CARBON ZEOLITE
IMPREGNATION
HYDROXIDE PRECIPITATION
CALCINING
PACKAGING
1000 SUPPORTED OXIDE CATALYST (5-15% ACTIVE MATERIAL)
THIS STEP OMITTED WHEN NITRATE SALT IS USED
DUSTS
OFF-SPECIFICATION PRODUCT
WASTE:
SPILLAGE
1 METAL (AS SALT) WATER
CAUSTIC WASTE
FLOOR SWEEPINGS AND VACUUM CLEANINGS
<0.1 METAL OXIDE MISC. TRASH
SOLIDS
5 METAL OXIDE 45 SUPPORT MATERIAL
TREATMENT:
PRECIPITATION, FILTRATION
NONE
NONE
DISPOSAL:
DISCHARGE LIQUID, REPROCESS OR SELL SOLIDS
LANDFILL
REPROCESS OR SELL

FIGURE 5-74

MANUFACTURE OF SUPPORTED METAL OXIDE CATALYST MATERIALS

5.5.6.1 Aggregate of Hazardous Wastes from SIC 28198 Destined for Land Disposal

No problems of hazardous wastes destined for land disposal were found from the manufacture of inorganic catalyst materials. The practice of reclaim of metals is followed throughout this industry.

5.5.6.2 Projection of Hazardous Wastes from SIC28198 Destined for Land Disposal

No process changes are anticipated in this industrial segment that would generate land-destined hazardous wastes, nor are air and water regulations expected to do so.

5.5.7 Other Industrial Inorganic Chemicals, Not Elsewhere Classified (SIC 28199)

5.5.7.1 Activated Carbon

As shown in Figure 5-75, activated carbon and charcoal are prepared by calcination of material products (coconut shells, etc.). The by-product gases from these operations are normally combusted. All wastes are waterborne, none are land disposed.

5.5.7.2 Ammonium Compounds

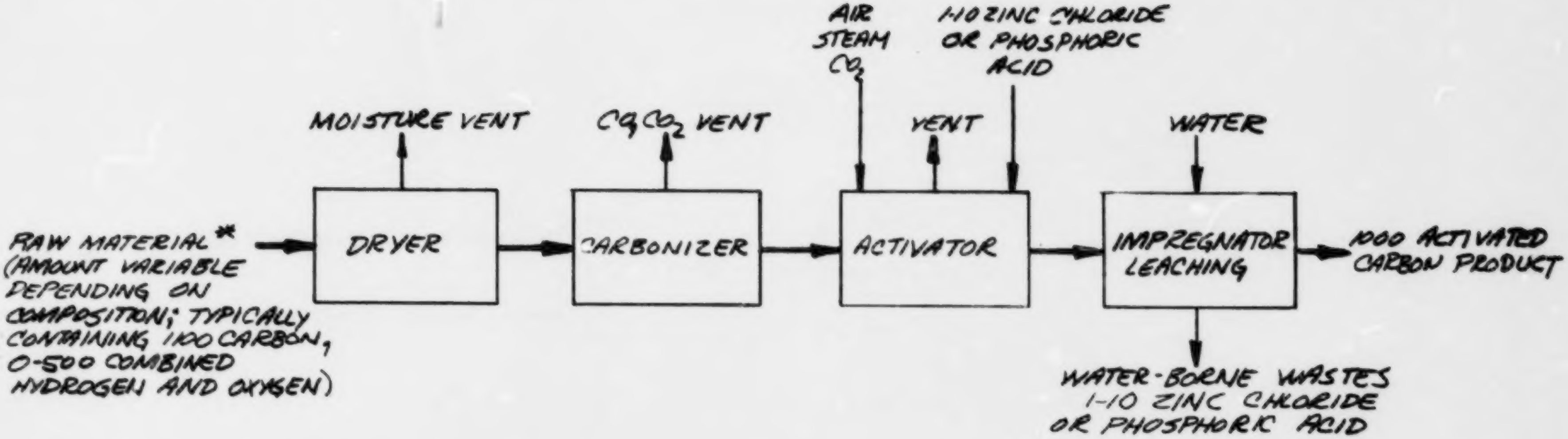
Ammonium hydroxide is made by dissolution of ammonia in water under pressure. There are no solid wastes generated, and other wastes consist only of spills or bottle breakage of ammonia solution. A flow diagram is shown in Figure 5-76.

Ammonium chloride is recovered as a by-product from Solvay process soda ash manufacture. There are no hazardous wastes generated. The flow diagram is given in Figure 5-77.

5.5.7.3 Arsenic Oxides (As_2O_3)

This material is produced as shown in Figure 5-78. Flue dusts from copper smelter operations are collected by bag filtrations and electrostatic precipitators from smelter vent gases. These dusts are then roasted to sublimate arsenic oxide, which is then collected in cooled chambers.

All vent gases from this process are subjected to bag filtration and electrostatic precipitation systems and all dusts collected are recycled to the process. No hazardous wastes are generated.



*PETROLEUM COKE, SAWDUST, LIGNITE, COAL, PEAT, WOOD, CHARCOAL, NUT SHELLS OR FRUIT PITS

FIGURE 5-75
ACTIVATED CARBON MANUFACTURE

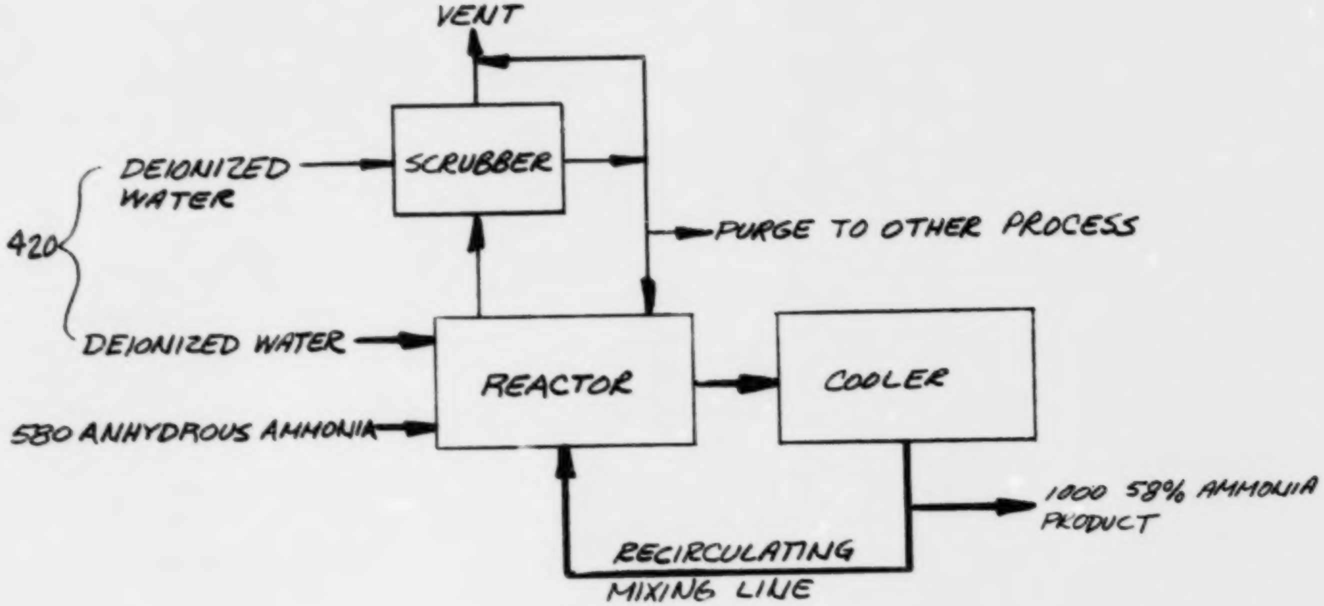


FIGURE 5-76
AMMONIUM HYDROXIDE MANUFACTURE

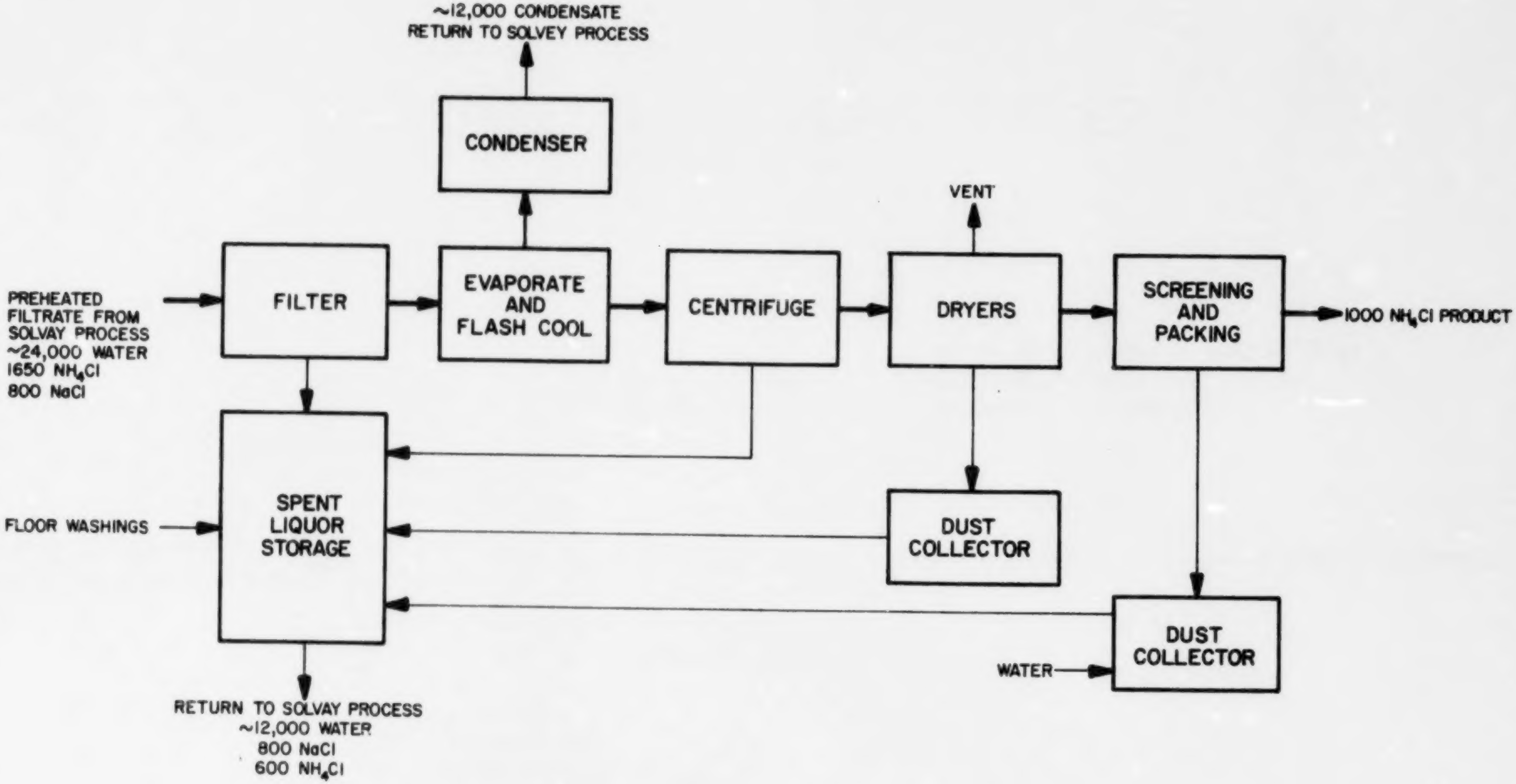


FIGURE 5-77
AMMONIUM CHLORIDE MANUFACTURE
FROM SOLVAY PROCESS WASTES

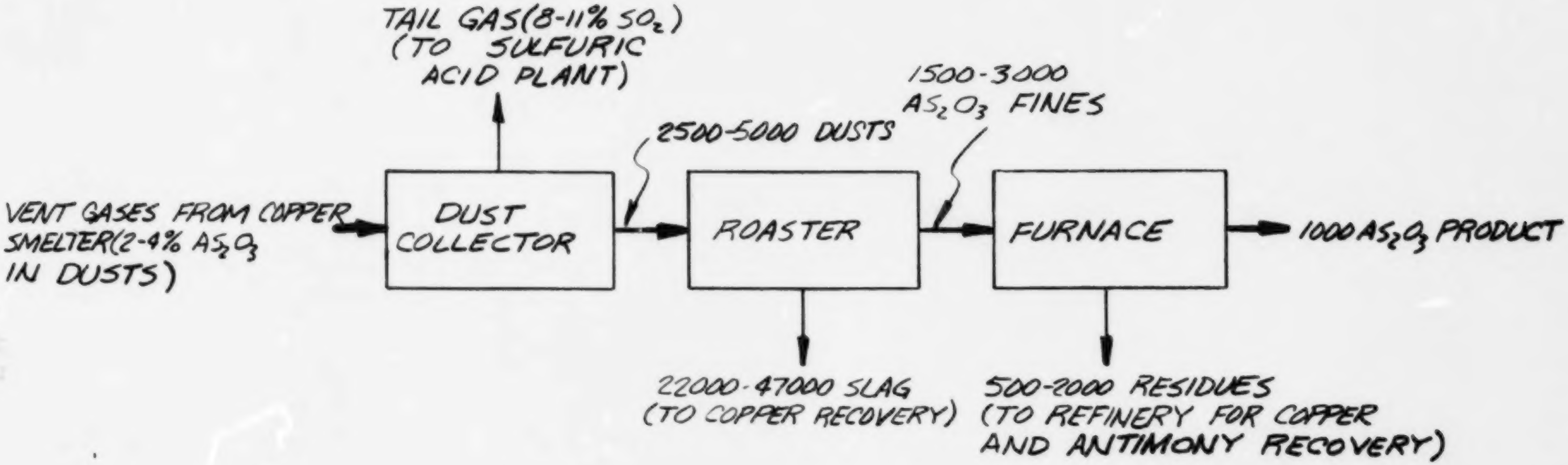


FIGURE 5-78

MANUFACTURE OF ARSENIC OXIDES

5.5.7.4 Barium Compounds

Barium salts are made directly or indirectly from barite ores which are first reduced to sulfide. The sulfide is then converted to other salts by chemical reaction. For example, reaction with either soda ash or CO_2 under pressure is used to produce the carbonate. The flow diagram for this is shown in Figure 5-79. Reaction with sodium sulfate is used to make purified $BaSO_4$.

Most of the wastes from all of these processes are waterborne and barium is removed from them by precipitation as the sulfate. Sulfide wastes from these processes are also largely waterborne and are treated either by aeration or chemical precipitation with iron salts. The iron sulfide (formed in the latter case) is insoluble and not hazardous. Treatment by oxidation produces thiosulfates and sulfates in solution, which are not hazardous. Small amounts of residual sulfide remain after treatment.

The solid wastes generated by these processes are barium sulfate (which sometimes is reused) and, in some cases, insoluble iron sulfide. These are not hazardous and Appendix A discusses these constituents.

5.5.7.5 Beryllium Compounds

There are three beryllium compounds produced commercially: the hydroxide, the oxide, and the metal. Only two U.S. facilities are involved. Beryl ore (beryllium aluminosilicate) is leached with sulfuric acid to dissolve the aluminum and beryllium contents. A solid waste of inert silica results here, but this waste is non-hazardous. Next, the solution of aluminum and beryllium sulfates is partially evaporated causing the aluminum sulfate to crystallize out. This material is then collected, slurried with water, and discharged as a waterborne waste. The beryllium sulfate solution is reacted with caustic to precipitate $Be(OH)_2$, which is then recovered as product. The sodium sulfate formed is discarded as a waterborne waste. The flow diagram is given in Figure 5-80.

To produce the oxide, the hydroxide is redissolved in sulfuric acid, treated with purification agents to remove iron salts as a solid waste (FeS), reconverted to the hydroxide, and calcined. The remainder of the wastes are water-borne. The flow diagram is shown in Figure 5-81.

In the production of beryllium metal, the hydroxide is first converted to ammonium beryllium fluoride, which is pumped, and decomposed to BeF_2. The fluoride is then recovered as a

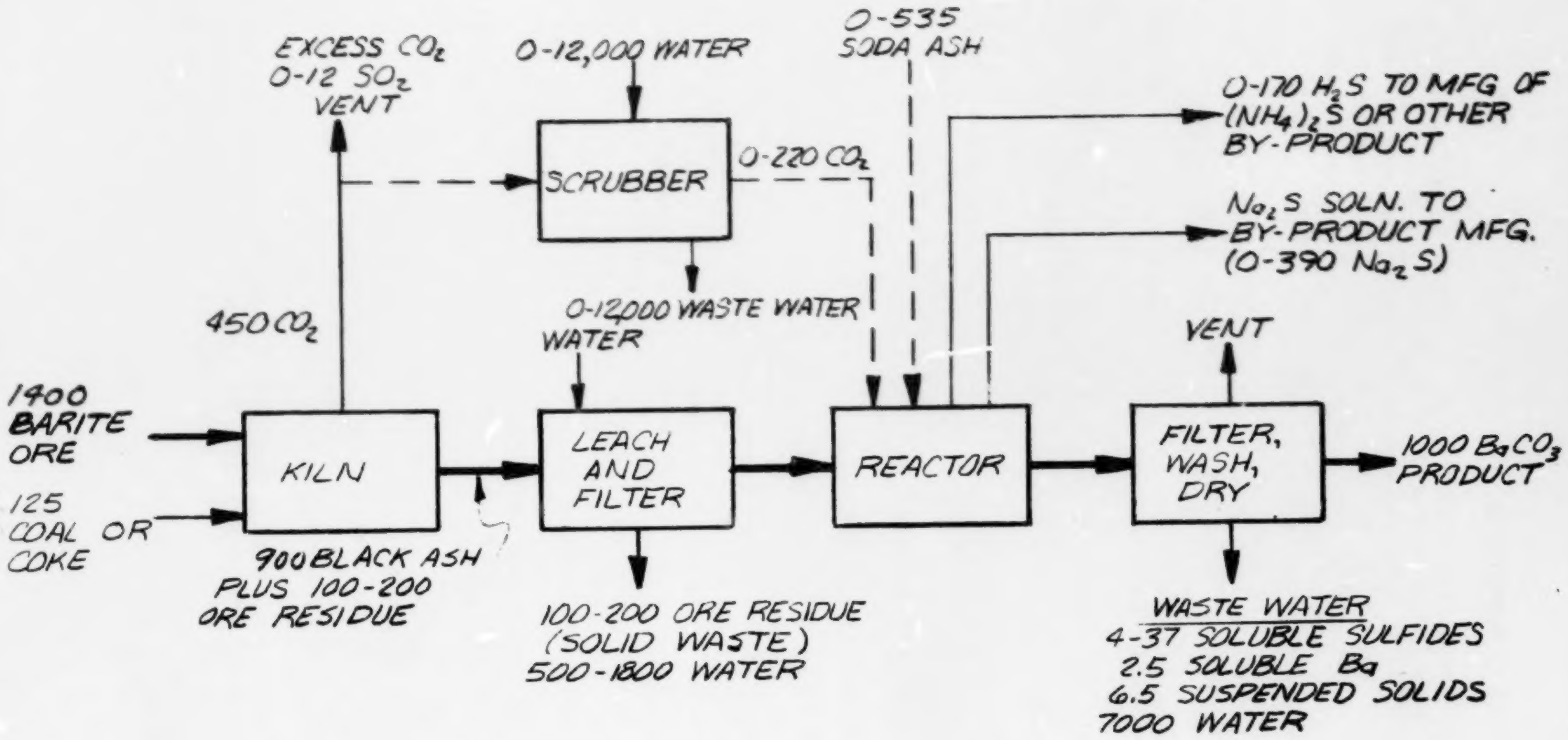


FIGURE 5-79

BARIUM CARBONATE MANUFACTURE

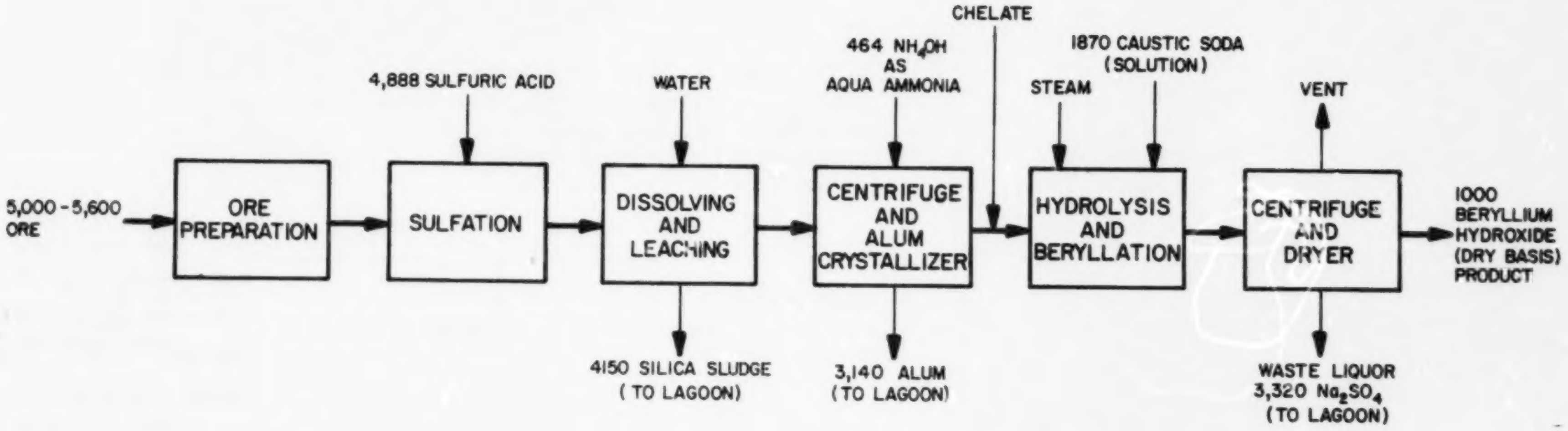

5,000 - 5,600 ORE
ORE PREPARATION
4,888 SULFURIC ACID
SULFATION
WATER
DISSOLVING AND LEACHING
4150 SILICA SLUDGE (TO LAGOON)
464 NH$_4$OH AS AQUA AMMONIA
CENTRIFUGE AND ALUM CRYSTALLIZER
3,140 ALUM (TO LAGOON)
CHELATE
STEAM
1870 CAUSTIC SODA (SOLUTION)
HYDROLYSIS AND BERYLLATION
VENT
CENTRIFUGE AND DRYER
WASTE LIQUOR 3,320 Na$_2$SO$_4$ (TO LAGOON)
1000 BERYLLIUM HYDROXIDE (DRY BASIS) PRODUCT

FIGURE 5-80
BERYLLIUM HYDROXIDE MANUFACTURE

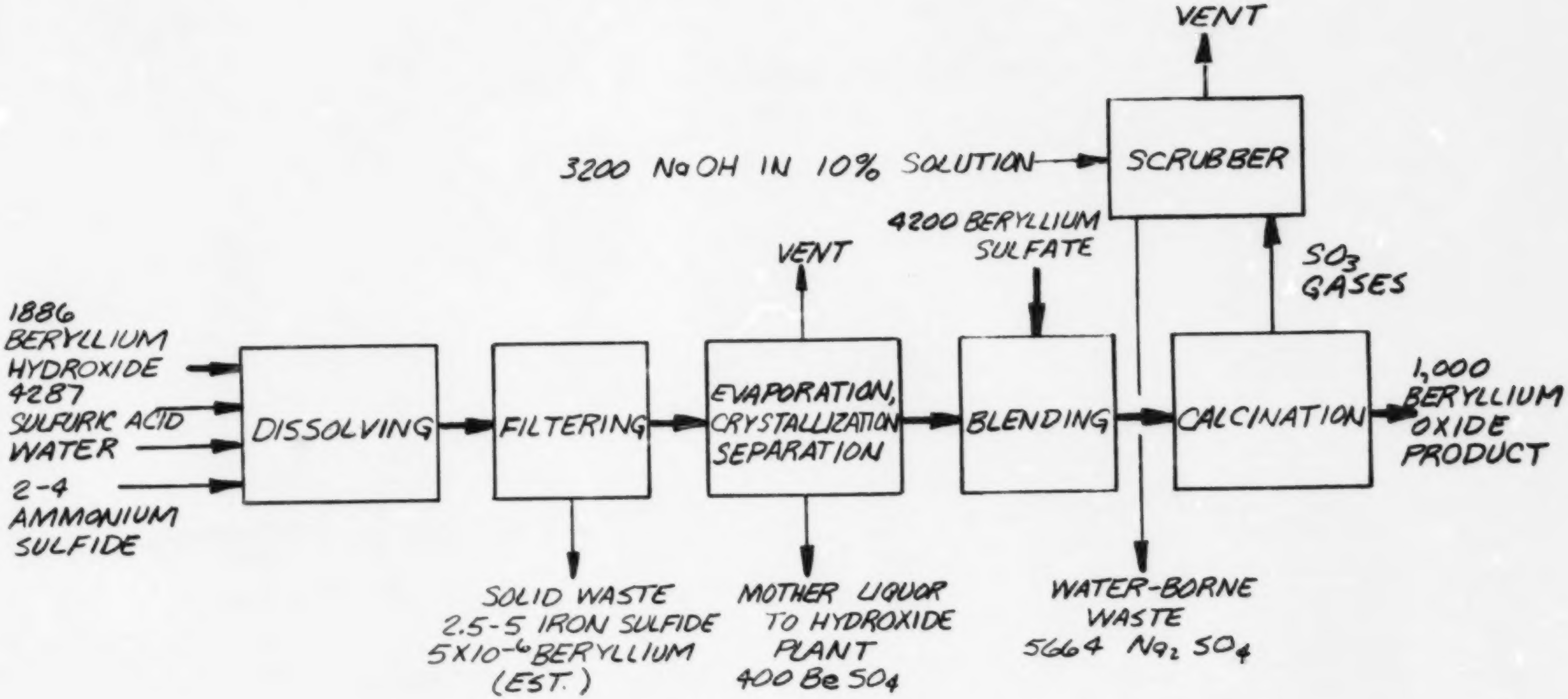

1886 BERYLLIUM HYDROXIDE
4287 SULFURIC ACID
WATER
2-4 AMMONIUM SULFIDE
DISSOLVING
FILTERING
SOLID WASTE 2.5-5 IRON SULFIDE 5X10-6 BERYLLIUM (EST.)
VENT
EVAPORATION, CRYSTALLIZATION SEPARATION
MOTHER LIQUOR TO HYDROXIDE PLANT 400 Be SO4
4200 BERYLLIUM SULFATE
BLENDING
3200 NaOH IN 10% SOLUTION
SCRUBBER
VENT
WATER-BORNE WASTE 5664 Na2 SO4
SO3 GASES
CALCINATION
1,000 BERYLLIUM OXIDE PRODUCT

FIGURE 5-81

BERYLLIUM OXIDE MANUFACTURE

solid and reacted in a furnace with magnesium. The product metal is then separated from the magnesium fluoride co-product which is discarded as a solid waste. This operation, however, is non-ferrous metallurgy--not included in SIC 281.

Current practice in the industry (based on plant visits) appears to involve lagooning of all of the wastes listed above. Lagoon effluent waters are lime treated to minimize discharge of fluorides. There is no "significant" amount of beryllium compounds in the water-borne effluent. The properties of beryllium, beryllium oxide, and beryllium hydroxide are discussed in Appendix A. There are only two plants involved, and the hazardous wastes are the fluoride associated with beryllium metal production, which is not SIC 281 product operation.

5.5.7.6 Boron Halides

Boron trichloride is produced by reaction of chlorine, coke and boric oxide. The product emerges from the reactors as a gas, is purified, compressed, and packaged. The only wastes generated are a small amount of boric oxide from the reactor cleanout and from the scrubbing of vent gases. The latter are waterborne and the former are not hazardous. Figure 5-82 is a flow diagram for the chloride manufacture.

Currently there is only one producer of boron trifluoride. The details of the process in use are therefore proprietary. Hence no flow diagram is furnished. This process in general is the reaction of fluosulfonic acid and boric acid. The by-product is 99-100% sulfuric acid. All wastes associated with the process are in liquid form. This information was furnished by the manufacturer. Based on this it is judged that all wastes are discharged to water, and none are land disposed.

5.5.7.7 Bromine and Iodine

These chemicals are extracted from natural brines. In both cases chlorine gas is added to natural brines and this effects oxidation from iodide and bromide ions to free iodine and bromine. These are then air stripped from the chlorinated brine. There are no associated wastes as the spent brines are returned to their sources as shown in Figures 5-83 and 5-84. This constitutes effective recycle of wastes.

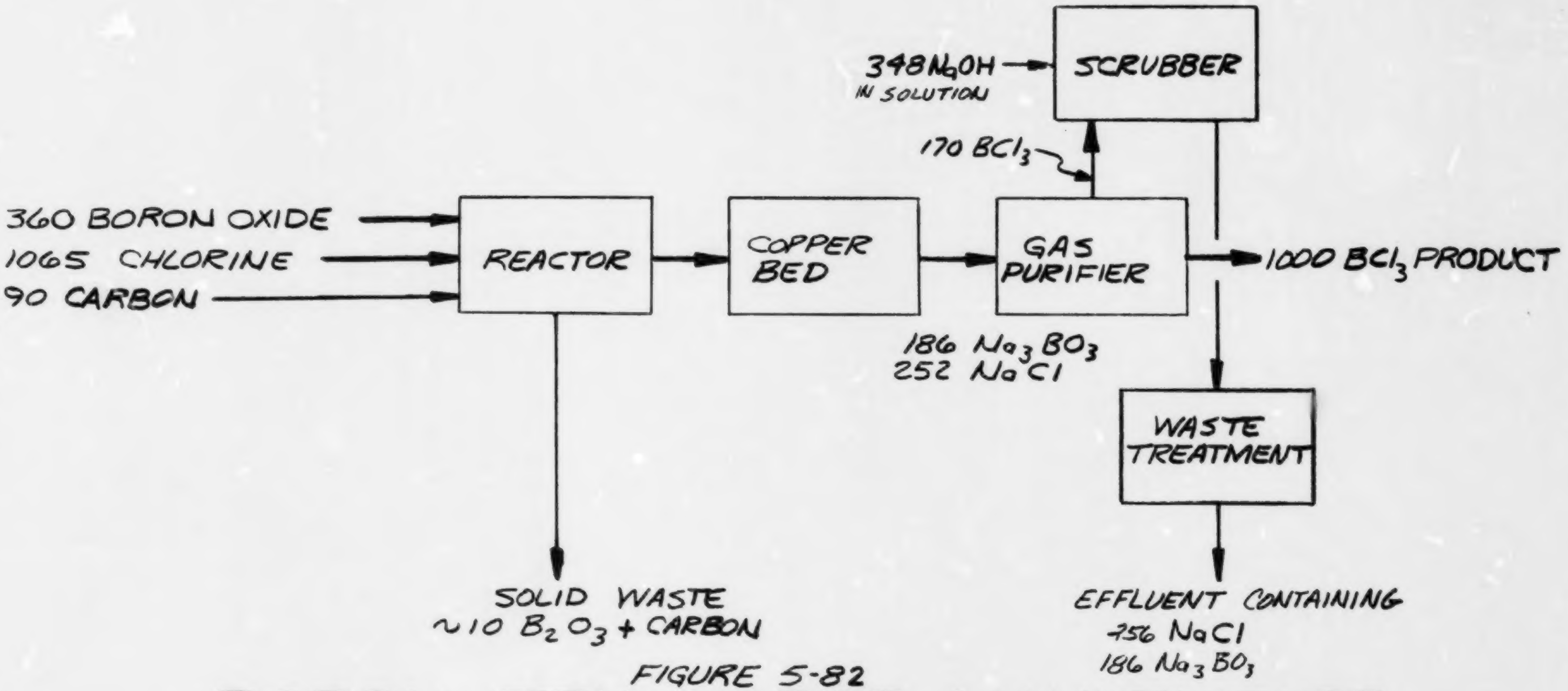


FIGURE 5-82
BORON TRICHLORIDE MANUFACTURE

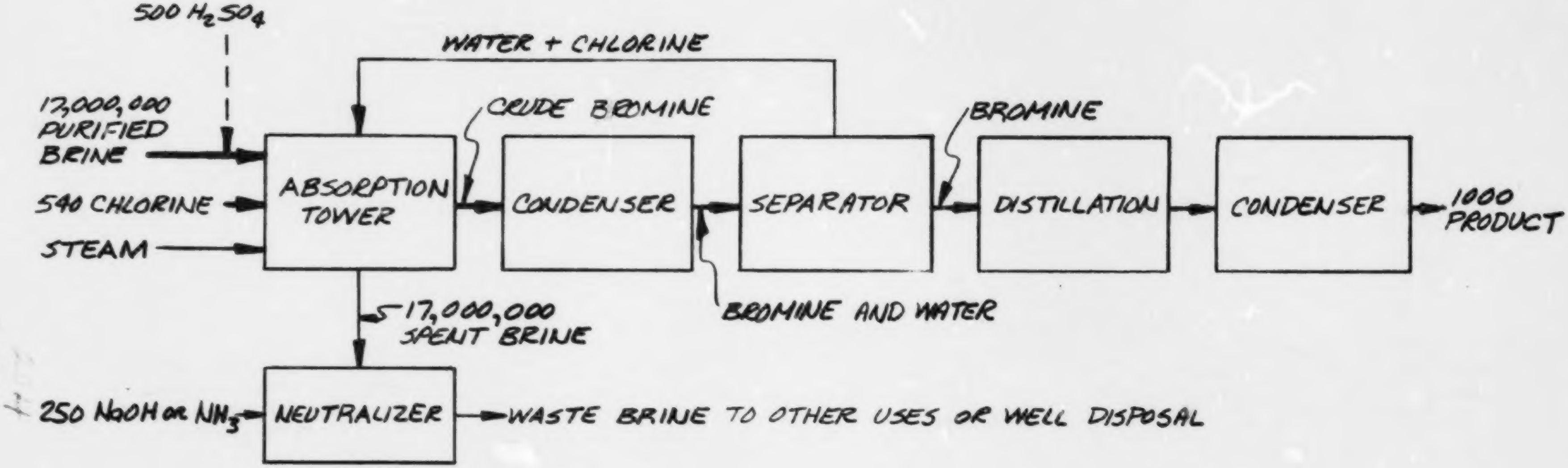


FIGURE 5-83
BROMINE MANUFACTURE

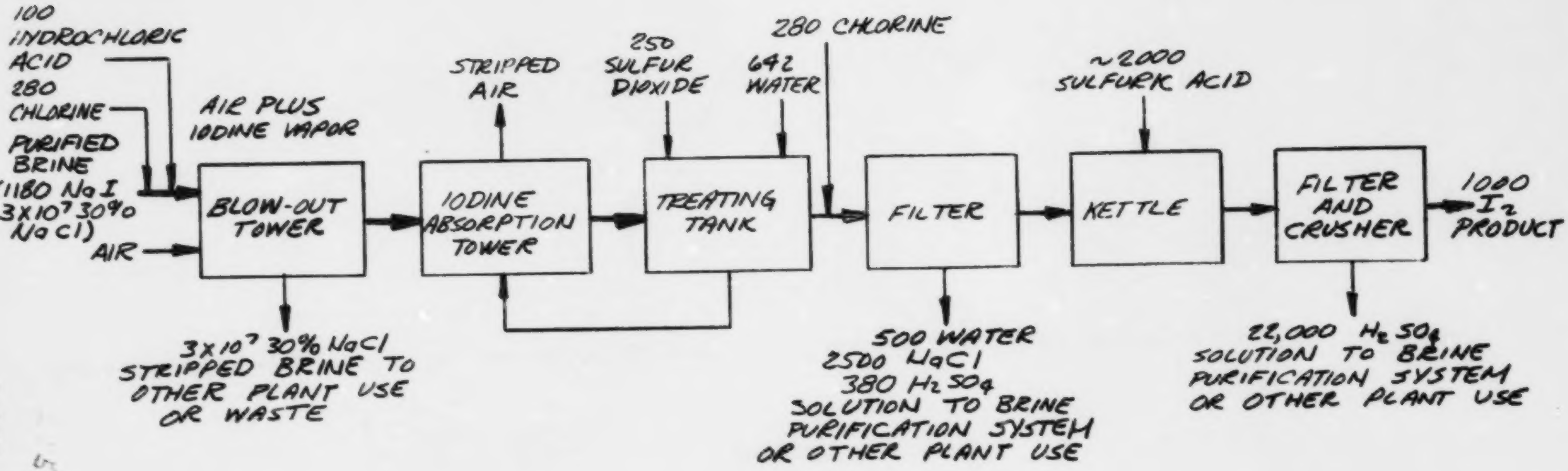


FIGURE 5-84
IODINE MANUFACTURE

5.5.7.8 Calcium Compounds

Calcium carbide is produced by thermal reaction of lime and coke in one of two varieties of furnace. In the case of the closed furnace, wastes arise from the use of wet dust collection equipment on the vent gases. The materials collected by dry collection equipment consist of lime and coke and are recycled. In the case of open furnaces, wet scrubbing or dry collection can be employed for the vent gases. This is shown in Figure 5-85. None of these wastes are hazardous.

As shown in Figure 5-86, calcium carbonate is prepared by reaction of calcium chloride with soda ash. The process wastes include significant amounts of unrecovered product which are settled out of wastewaters in lagoons. These wastes are not hazardous.

As shown in Figure 5-87, calcium carbonate is also produced. by reaction of slaked lime with carbon dioxide under pressure. No significant wastes arise from this process.

Lime (calcium oxide) is made by calcination of limestone in a continuous verticle or rotary kiln. After calcination, the calcium oxide is cooled and then packaged or crushed and screened to yield a pulverized product. It may be slaked by reaction with water to yield calcium hydroxide. The only solid wastes produced by either operation arise from the scrubbing of vent gases to remove particulates. In cases where dry bag collection is used, some, if not all of the recovered materials can be recycled to the process. Where wet collection methods are utilized, solids are frequently removed from scrubber waters in settling lagoons. These wastes are not hazardous. The operations are shown in Figures 5-88 and 5-89.

Calcium chloride is produced either by extraction from natural brines or recovered as a co-product from Solvay soda ash manufacture. In the manufacturing of calcium chloride from brine, the salts are solution mined and the resulting brines are first concentrated to remove sodium chloride by precipitation and then purified by the addition of other materials to precipitate sodium, potassium, and magnesium salts. The purified calcium chloride brine is then evaporated to yield a wet wolid which is flaked and calcined to a dry solid product. Extensive recycling of partially purified brine is used to recover most of the sodium chloride values. There are no solid wastes generated by either process, and the waterborne wastes are not hazardous. The recovery from natural brines is shown in Figure 5-90.

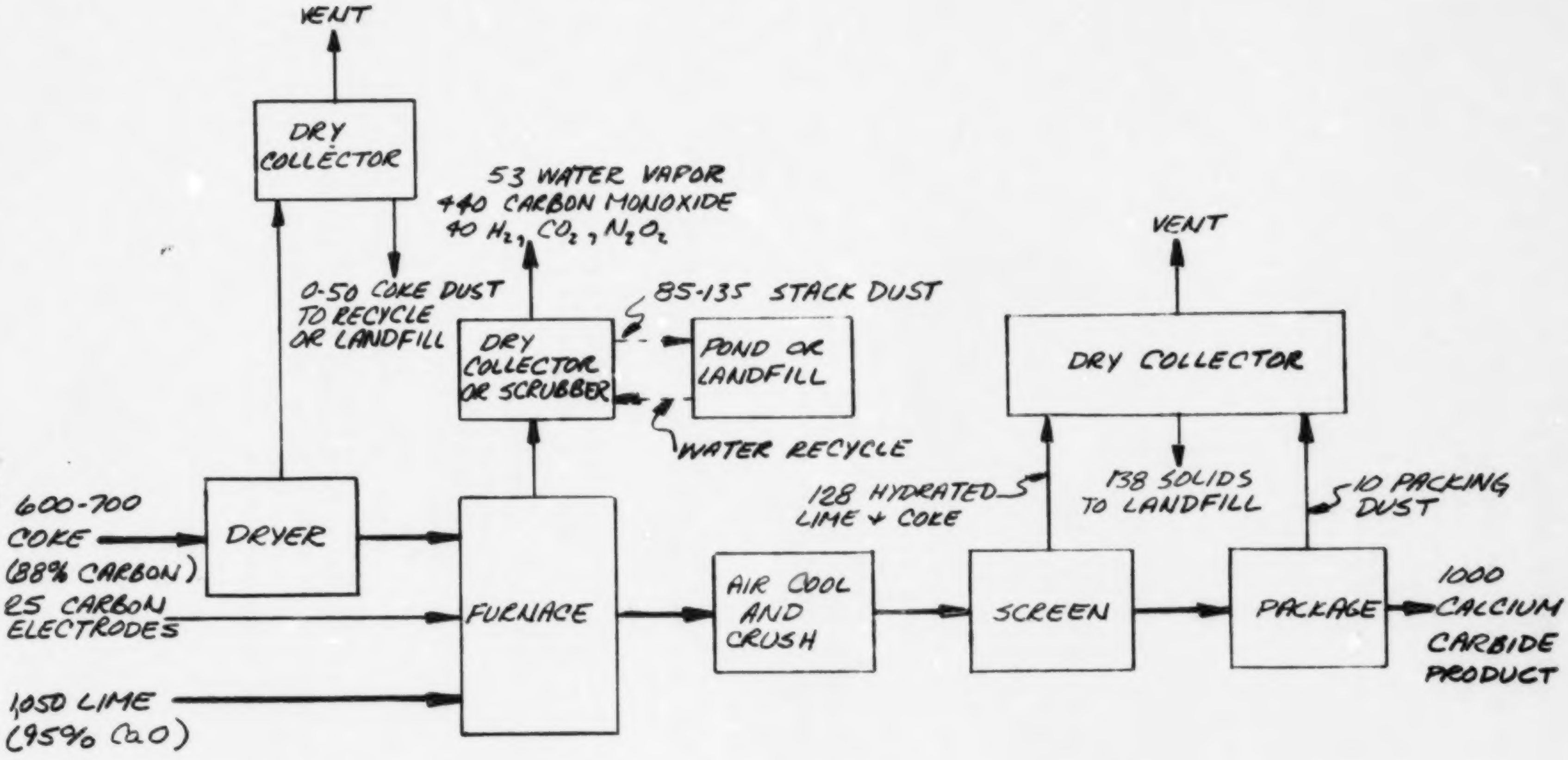


FIGURE 5-85

OPEN FURNACE CALCIUM CARBIDE MANUFACTURE

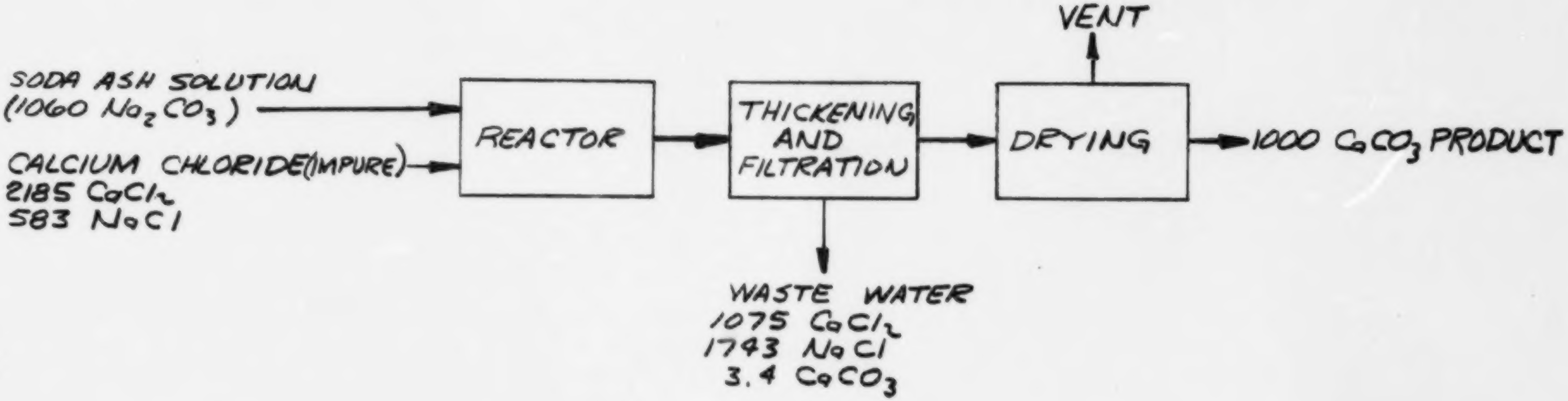


FIGURE 5-86
CALCIUM CARBONATE MANUFACTURE FROM CALCIUM CHLORIDE

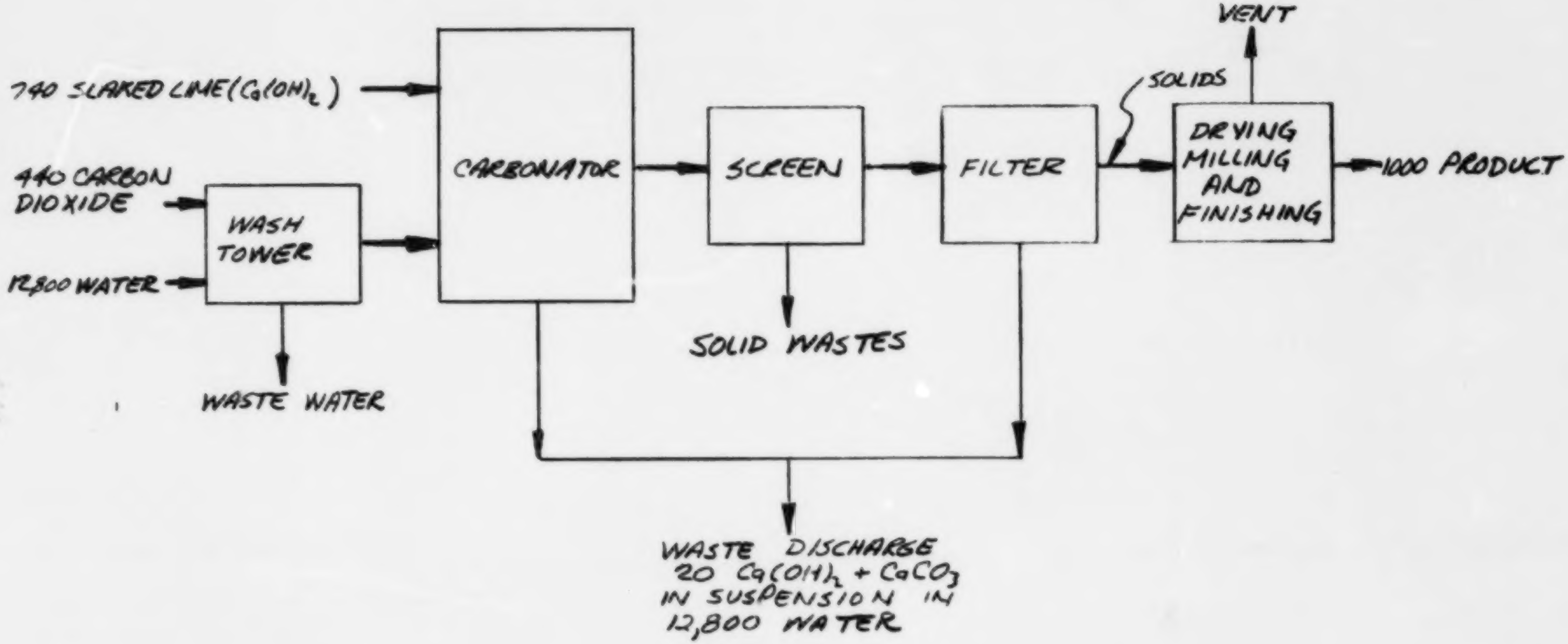


FIGURE 5-87
CALCIUM CARBONATE MANUFACTURE FROM SLAKED LIME

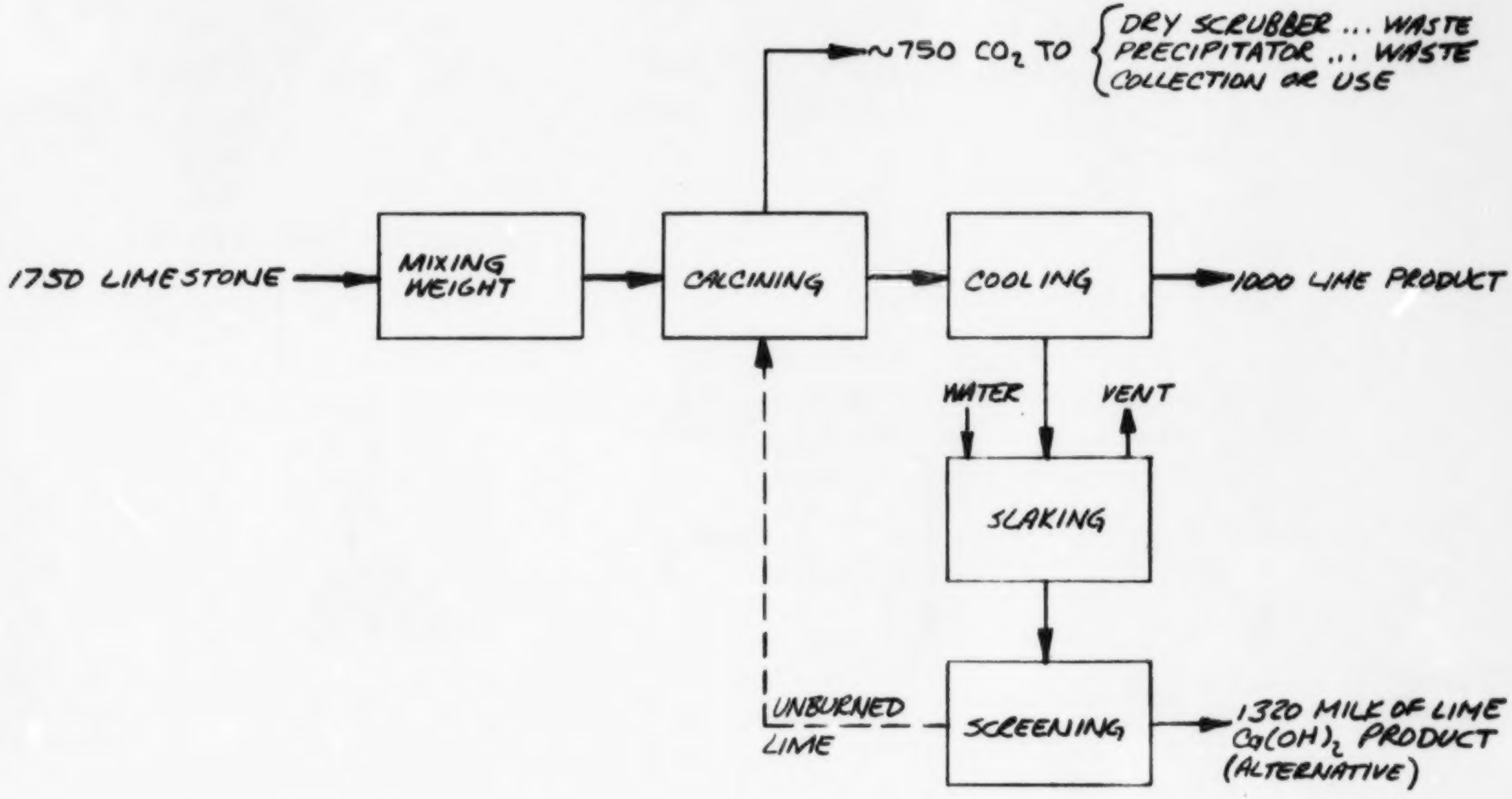


FIGURE 5-88

CALCIUM OXIDE (LIME) MANUFACTURE

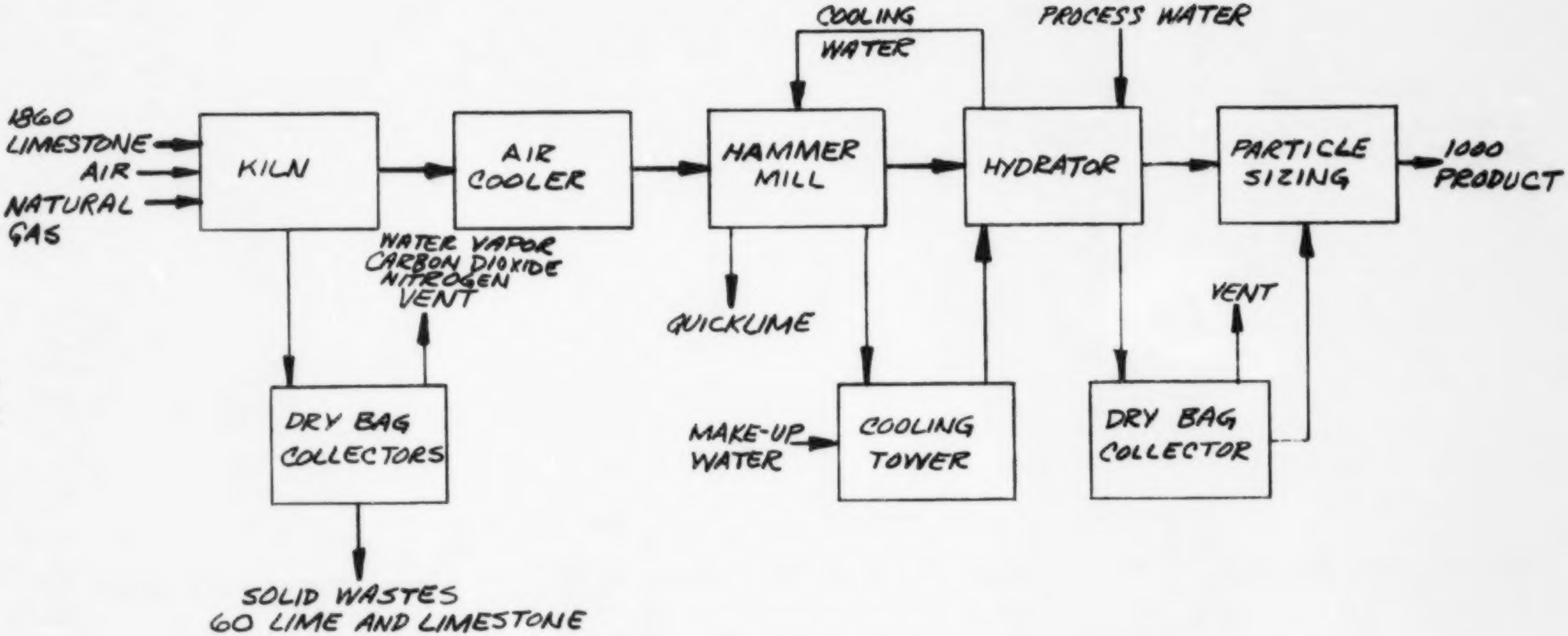


FIGURE 5-59

CALCIUM HYDROXIDE MANUFACTURE

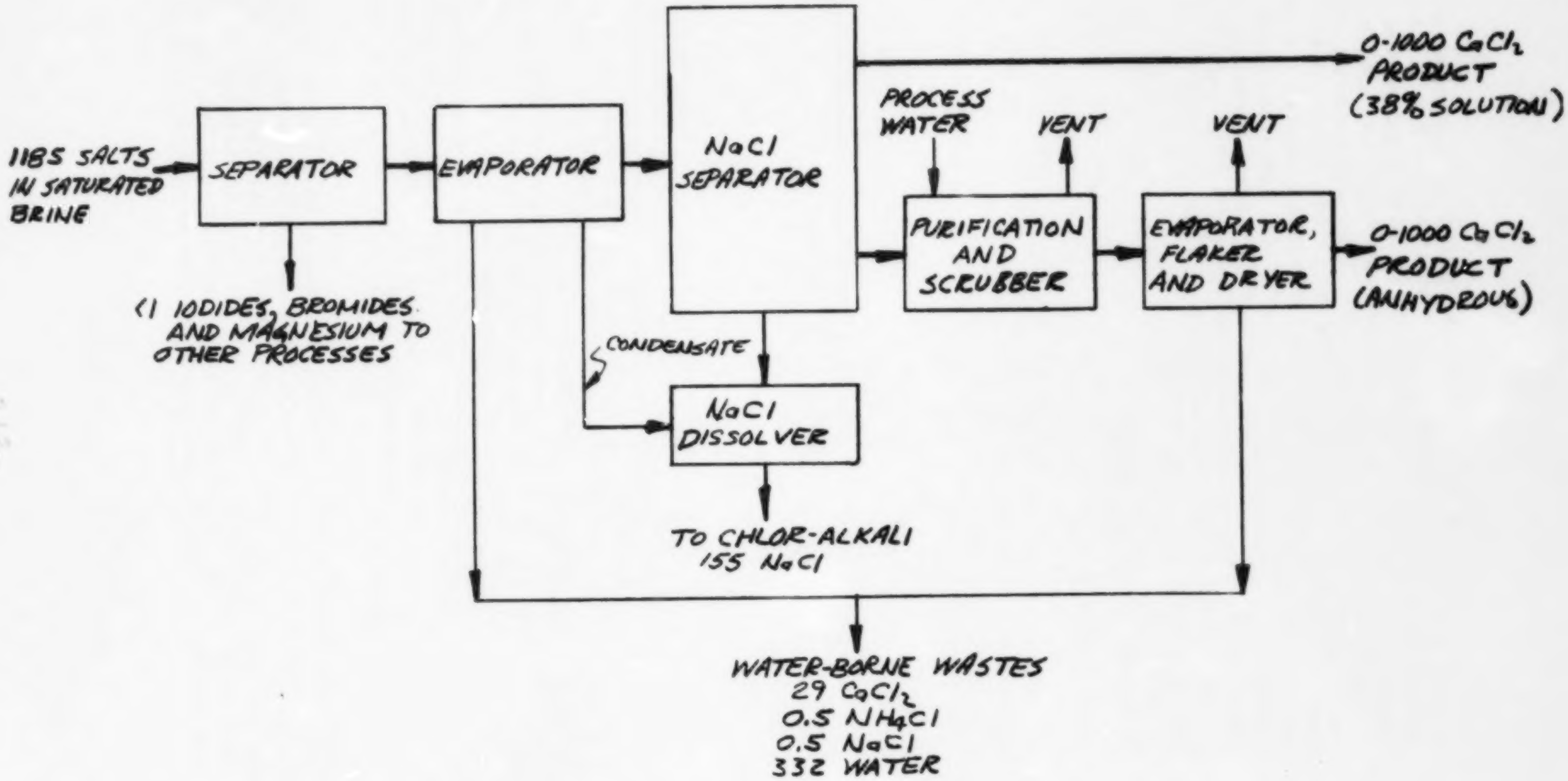

1lBS SALTS IN SATURATED BRINE
SEPARATOR
<1 IODIDES, BROMIDES AND MAGNESIUM TO OTHER PROCESSES
EVAPORATOR
CONDENSATE
NaCl SEPARATOR
NaCl DISSOLVER
TO CHLOR-ALKALI 155 NaCl
0-1000 CaCl2 PRODUCT (38% SOLUTION)
PROCESS WATER
VENT
PURIFICATION AND SCRUBBER
VENT
EVAPORATOR, FLAKER AND DRYER
0-1000 CaCl2 PRODUCT (ANHYDROUS)
WATER-BORNE WASTES
29 CaCl2
0.5 NH4Cl
0.5 NaCl
332 WATER

FIGURE 5-90

CALCIUM CHLORIDE MANUFACTURE

The principal SIC 281 calcium phosphate products are food-grade and animal-feed-grade materials. The processes are shown in Figures 5-91 and 5-92. With food-grade calcium phosphate, high purity phosphoric acid is used and no hazardous wastes are produced. The only solid waste is calcium phosphate, an edible material in pure form. In feed-grade preparation, land disposed wastes in small amounts containing calcium fluoride are generated. This material is "moderately hazardous" (see Appendix A for calcium fluoride), but the amounts in this waste stream are so small that the waste stream is not judged to be hazardous.

5.5.7.9 Cadmium Salts

Most commercially produced soluble cadmium salts (chloride, nitrate, sulfate) are produced by dissolution of the metal in the appropriate mineral acid, followed by evaporation of the solution to recover the desired products. Ordinarily there are no solid wastes generated as pure cadmium is the starting material.

Cadmium oxide is produced in a two step process from the sulfate. First, an aqueous solution of the sulfate is reacted with caustic and the insoluble hydroxide formed is recovered by filtration. The hydroxide is then calcined to the oxide. There are two sources of wastes from this process:

(a) Spent aqueous solutions from the precipitation traces of unrecovered cadmium. Treatment of these will generate minor amounts of cadmium sludges which exhibit properties described for cadmium hydroxide in Appendix A. This is a hazardous waste and requires stringent safeguards to permanently isolate the material.

(b) Dusts from the calcination process are normally collected by bag filtration methods and recycled. If not recycled, cadmium oxide dust is a potential candidate for land disposal and would require a secure landfill. The properties of cadmium oxide are detailed in Appendix A. The wastes mentioned here are very small and occur only in a few facilities.

Cadmium sulfide is produced as shown in Figure 5-93. By reacting a soluble cadmium salt in solution with sodium sulfide, the product is recovered by filtration. All of the wastes are initially water-borne, and treatment of these generates very small amounts of solids (primarily cadmium hydroxide). $Cd(OH)_2$ is a hazardous material; its properties

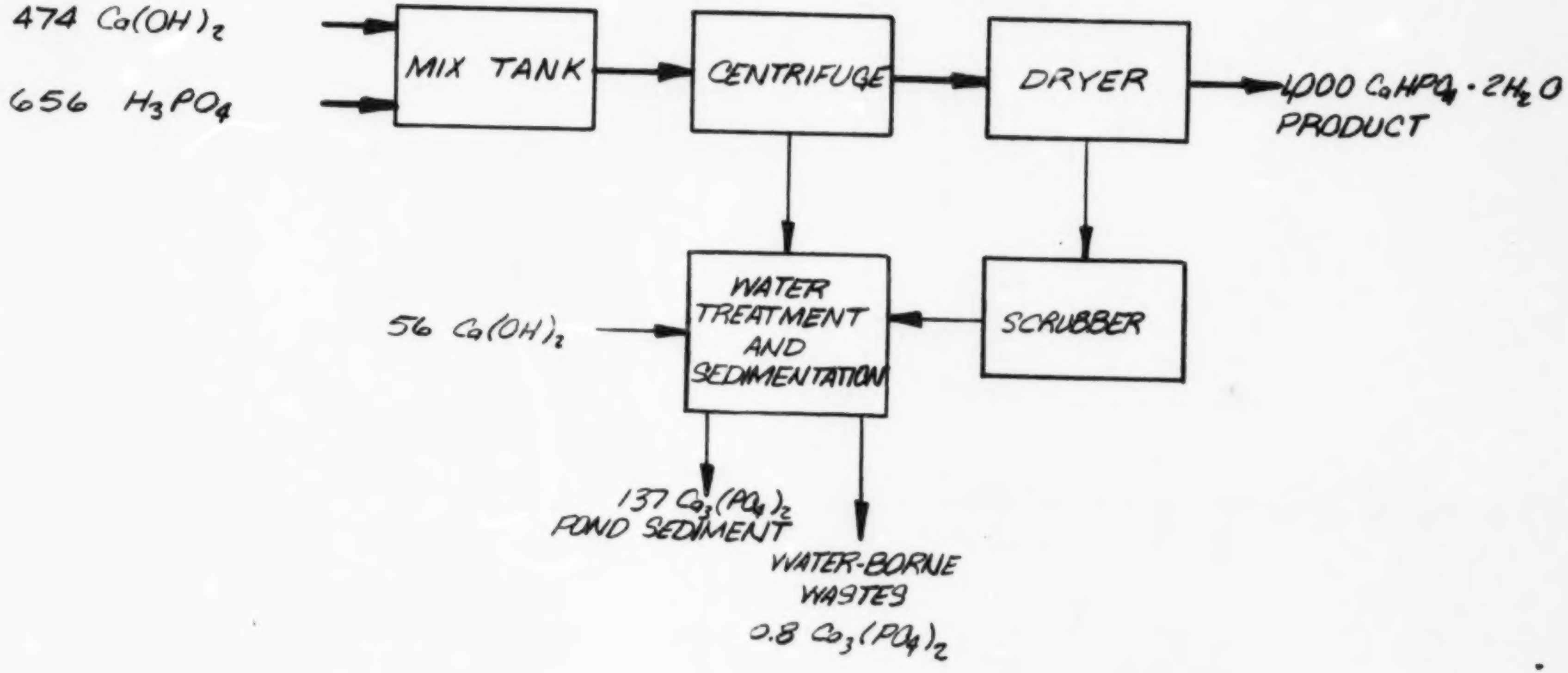

474 $Ca(OH)_2$
656 H_3PO_4
MIX TANK
CENTRIFUGE
DRYER
4000 $CaHPO_4 \cdot 2H_2O$ PRODUCT
56 $Ca(OH)_2$
WATER TREATMENT AND SEDIMENTATION
SCRUBBER
137 $Ca_3(PO_4)_2$ POND SEDIMENT
WATER-BORNE WASTES 0.8 $Ca_3(PO_4)_2$

FIGURE 5-91
MANUFACTURE OF FOOD GRADE CALCIUM PHOSPHATE

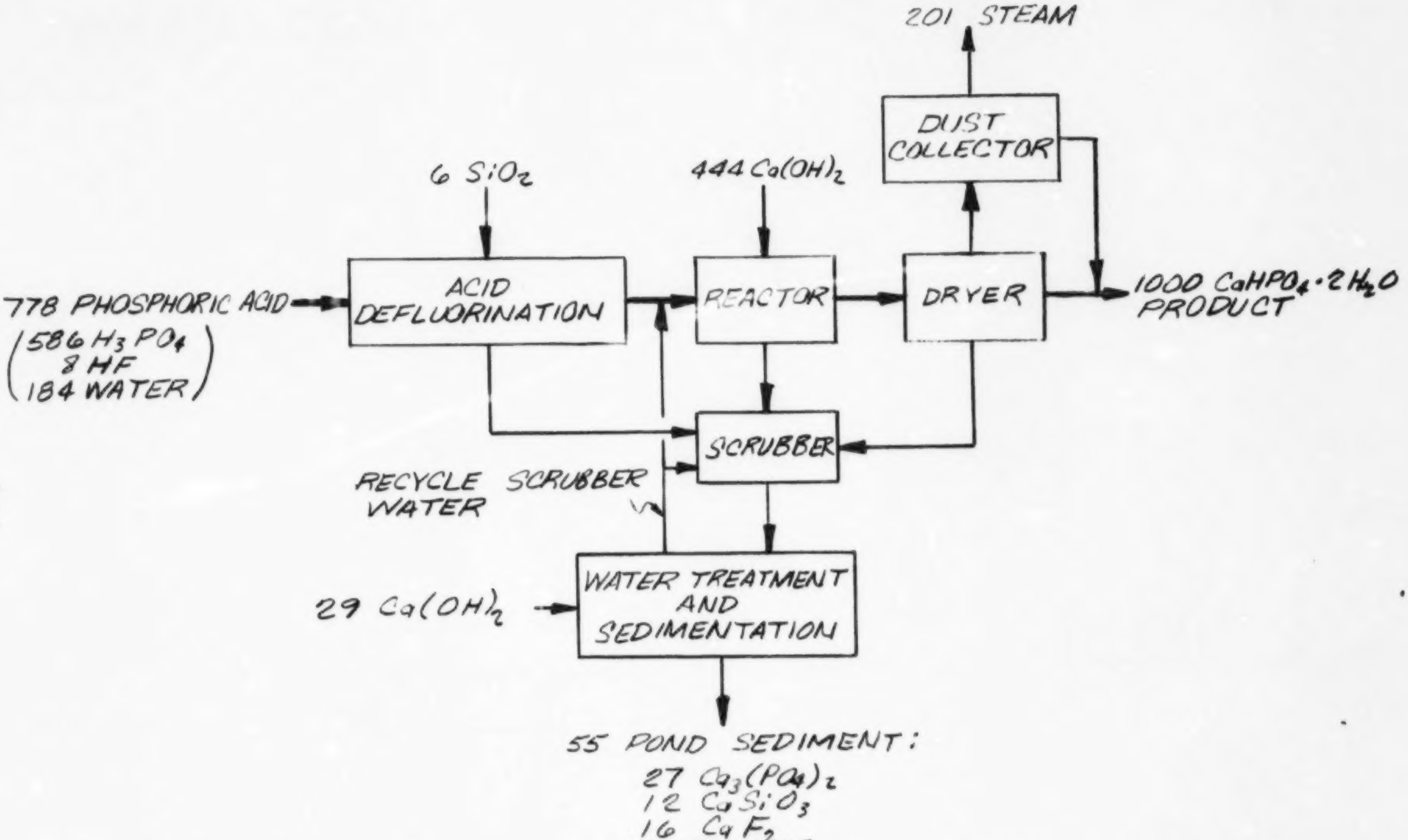


FIGURE 5-92

MANUFACTURE OF ANIMAL-FEED GRADE CALCIUM PHOSPHATE

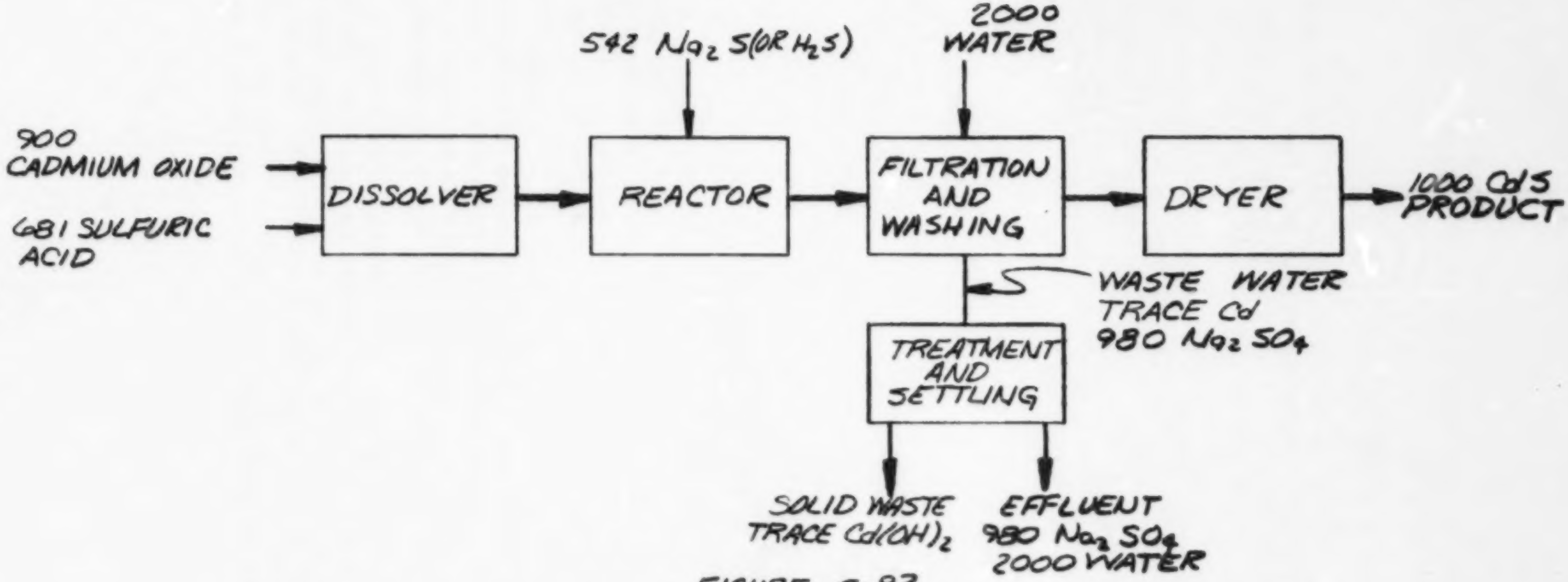


FIGURE 5-93

CADMIUM SULFIDE MANUFACTURE

are detailed in Appendix A. However, the amounts of material discarded from this industry are so small as to be insignificant.

5.5.7.10 Chromates

This group of materials includes sodium and potassium chromate and dichromate and chromic acid. Chromic acid is included because it is made from dichromates in dichromate plants, although it is in SIC 28194.

As shown in Figure 5-94, sodium dichromate is prepared by calcining a mixture of chrome ore, soda ash and lime, followed by water leaching and acidification of the soluble chromates. The insoluble residue from the leaching operation is recycled to leach out additional material prior to being discarded.

During the first acidification step, the chromate solution pH is adjusted to precipitate calcium salts. Further acidification converts it to the dichromate and a subsequent evaporation step crystallizes sodium sulfate (salt cake) out of the liquor. The sulfate is then dried and sold. The solutions remaining after sulfate removal are further evaporated to recover sodium dichromate. Chromic acid is produced from sodium dichromate by reaction with sulfuric acid. Sodium bisulfate is a by-product.

The bulk of the waste originates from the undigested portions of the ores used. These materials are mostly solid wastes contaminated with chromate. The wastes arising from spills and washdowns contain most of the hexavalent chromium. The wastes from water treatment and boiler blowdowns are principally dissolved sulfates and chlorides. The manufacture of chromic acid contributes no additional wastes.

The ore residues are contaminated with chromates. There are chromium-containing sludges from the wastewater treatment which constitute significantly hazardous waste streams. The properties of chromates are given in Appendix A.

Chromic acid plants are normally attached to dichromate facilities. The dichromate is reacted with sulfuric acid to precipitate chromic acid, which is then recovered by filtration. The sodium bisulfate by-product is usually reused in the dichromate plant. This process does not generate significant amounts of solid waste.

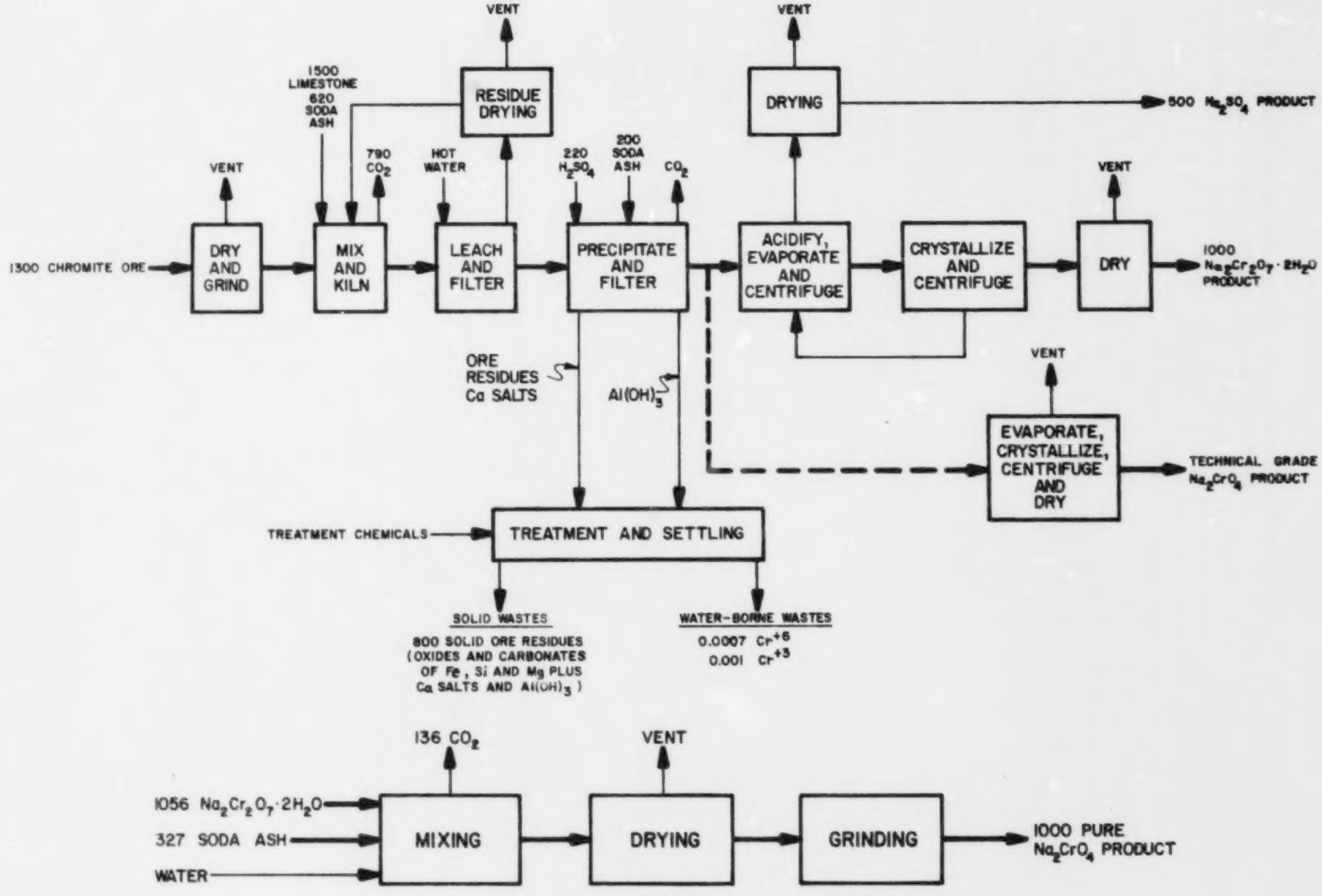


FIGURE 5-94
SODIUM DICHROMATE AND CHROMATE MANUFACTURE

As shown in Figure 5-95, potassium dichromate is made by the reaction in solution of potassium chloride and sodium dichromate. The solution is then pH adjusted, saturated, filtered and vacuum cooled to precipitate crystalline potassium dichromate which is recovered by centrifuging, dried, sized and packaged. The mother liquor from the product centrifuge is then concentrated to precipitate sodium chloride which is removed as a solid waste from a salt centrifuge. The resulting potassium dichromate solution is then evaporated to recover the product. The waste solid sodium chloride is contaminated with chromate salts, and is considered hazardous.

5.5.7.11 Chromic Salts

Chromic salts are produced by reaction of chromic oxide (Cr_2O_3) or hydroxide ($Cr(OH)_3$) with the appropriate mineral acids, followed by evaporation to recover the solid products. There are no wastes generated by these processes.

5.5.7.12 Cobalt Compounds

As shown in Figure 5-96, most of these compounds are produced by reaction of cobalt oxide with the appropriate acids. Except for small amounts of purification sludges, which are reprocessed to reclaim cobalt values, all of the wastes are water-borne. There are small amounts of cobalt in these. No hazardous wastes destined for land disposal were found.

5.5.7.13 Copper Compounds

As shown in Figure 5-97, copper sulfate is made by reaction of air, copper, and sulfuric acid. Either concentrated or dilute acid may be used. In general, the resulting solution is exposed to evaporation and a series of crystallization steps to obtain copper sulfate crystals, which are then centrifuged, air-dried, screened, and packaged for sale. The only solid wastes directly generated by the process are normally recycled to recover their copper values. A small amount of solid waste does arise in some cases due to treatment of wastewater from spills and leakages. This waste consists of small amounts of copper oxide but is insignificant in amount. Copper oxide properties are discussed in Appendix A.

Cuprous oxide is made by reaction of copper with air in a furnace or series of furnaces to form cupric oxide. The cupric oxide is then reduced in another furnace to cuprous oxide. Solid wastes are generally collected by bag filtration of vent gases and are recycled to the process. A

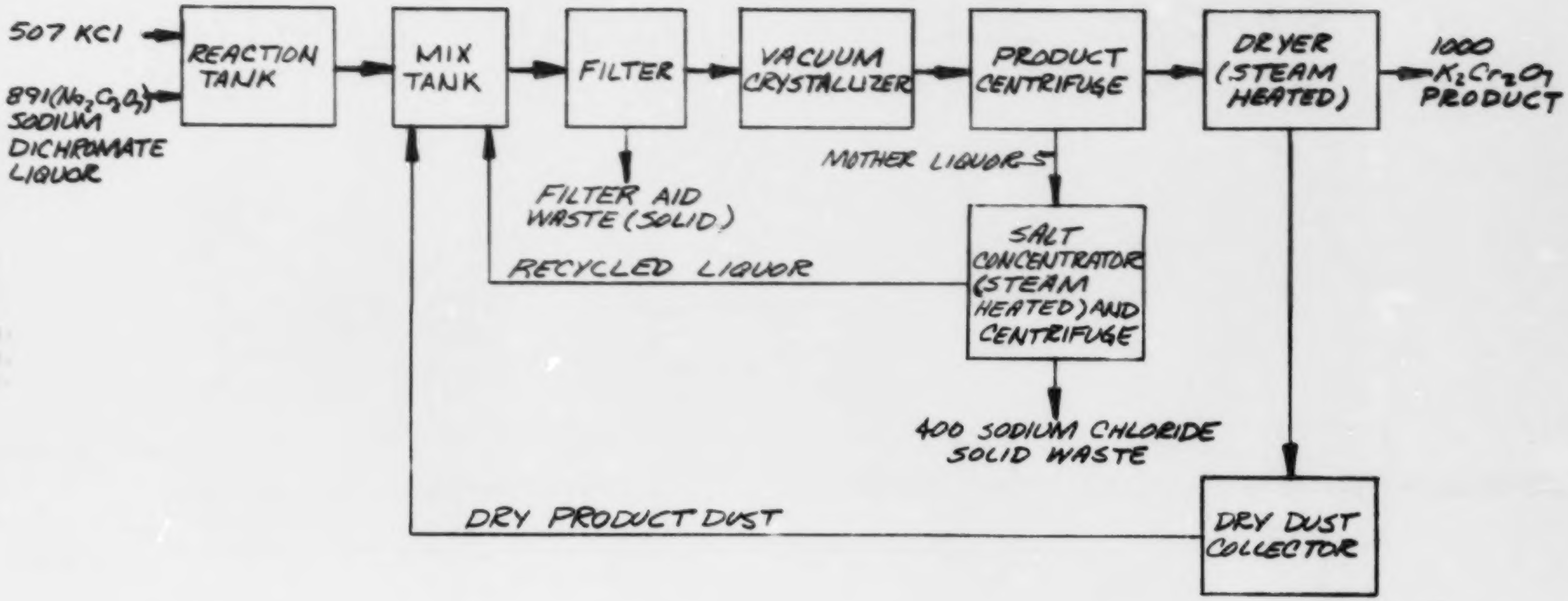


FIGURE 5-95

POTASSIUM DICHROMATE MANUFACTURE

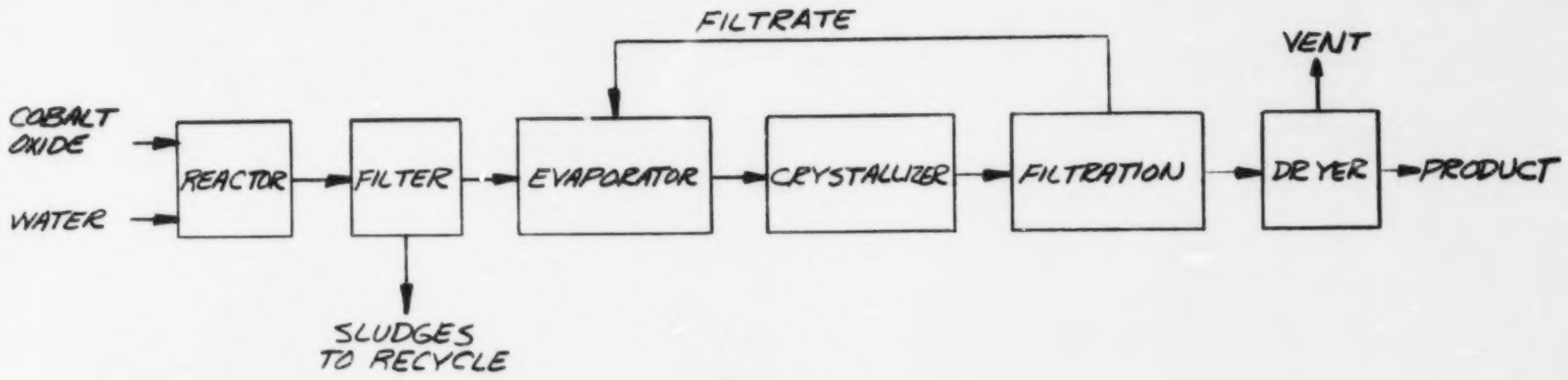


FIGURE 5-96
MANUFACTURE OF COBALT COMPOUNDS
(NITRATE, ACETATE, SULFATE, CHLORIDE)

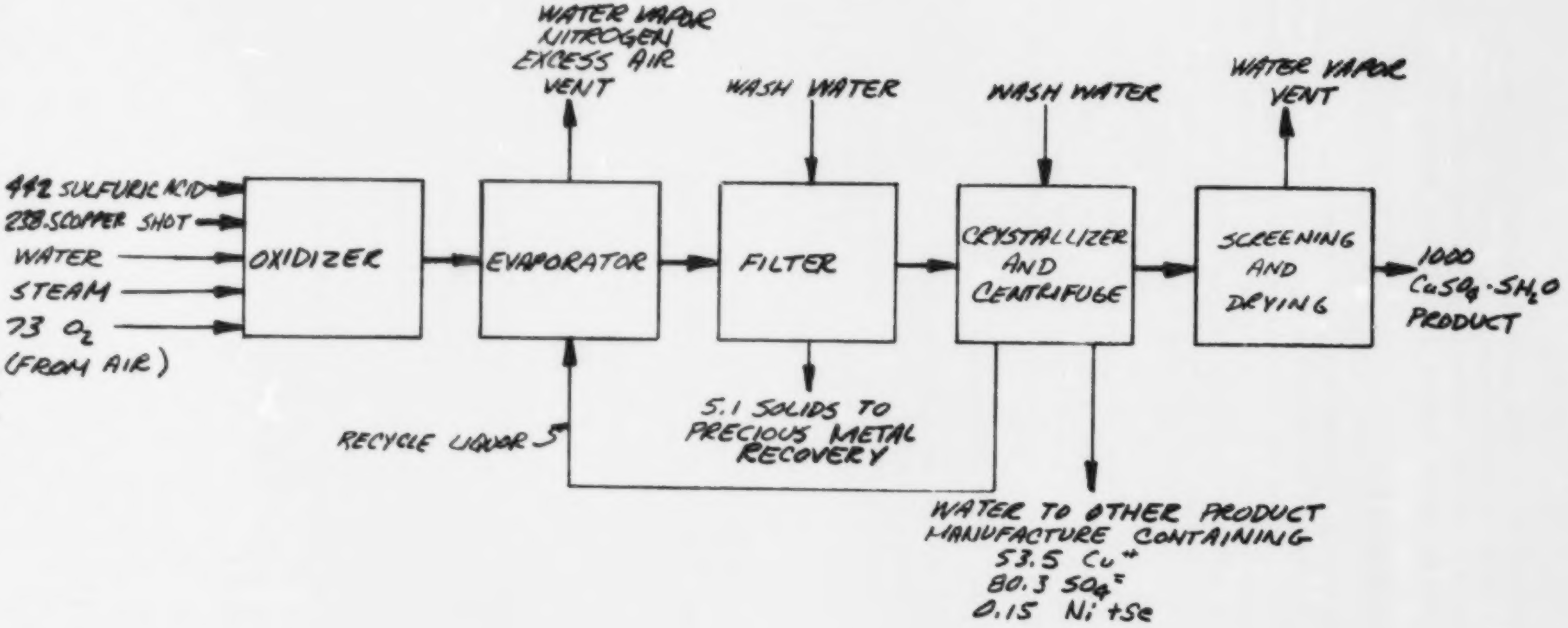


FIGURE 5-97
COPPER SULFATE MANUFACTURE

second method of production involves the anodic oxidation of copper in saline solutions. No solid wastes are generated in this case. Small amounts of water-borne wastes occur. The flow diagram is shown in Figure 5-98.

5.5.7.14 Fluorine

Most of the U.S. production of fluorine is produced in security classified amounts for the AEC. As shown in Figure 5-99, fluorine is produced by either electrolysis of molten potassium acid fluoride or liquid HF. Solid wastes may result from treatment of water-borne wastes, but no significant instances were found. Waterborne wastes are discharged or recovered. Future changes in process waste treatment involve the manufacture of HF solution for sale with the waste fluorides. Where caustic potash is used to scrub fluoride gases, the resultant potassium fluoride is recovered. This industrial segment was therefore not found to be a generator of hazardous wastes for land disposal.

5.5.7.15 Hydrogen Peroxide

Hydrogen peroxide is manufactured at six locations in the U.S. and a plant is on stand-by at a seventh. The principal method of manufacture (5 of the 6 producing plants) uses a cyclic organic process involving hydroquinone derivatives, as shown in Figure 5-100, called the "Reidl-Pfleiderer Process". No hazardous wastes are land disposed from this process.

The electrolytic process for hydrogen peroxide manufacture is based on sulfuric acid and ammonium sulfate raw materials. This process is operated at only one U.S. location, in the state of Washington. Contacts with industry have indicated that no new plants of this type are likely to be built. The plant brought off-stream in recent years to stand-by in Michigan is of this type. So far as is known there are no plans to remove the remaining operating electrolytic plant from production, but as its equipment becomes obsolete at some time in the future there is high likelihood that it would be. The process steps are shown in Figure 5-101. The sole land disposed hazardous waste is small quantities of iron cyanide compounds as sludges. It is estimated that less than 1.5 metric tons per year of these sludges are so disposed at this sole location. See Appendix A for properties of iron cyanides.

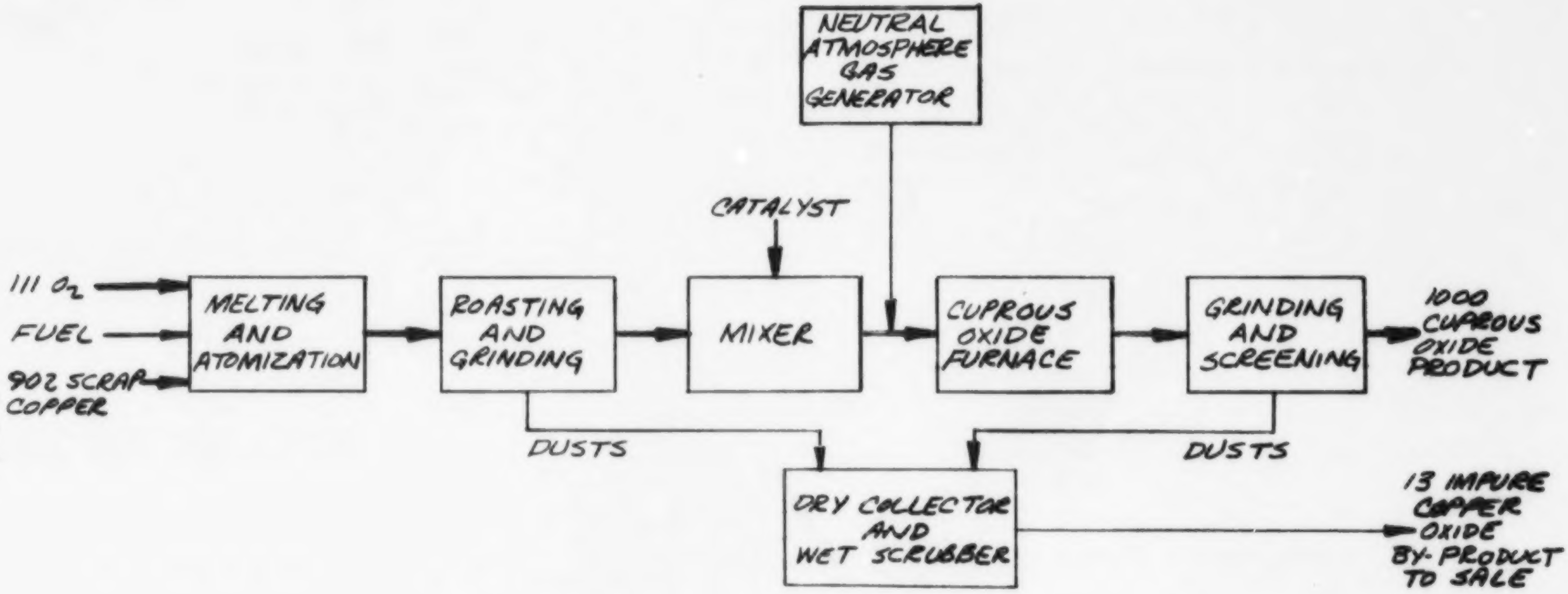


FIGURE 5-98
CUPROUS OXIDE MANUFACTURE

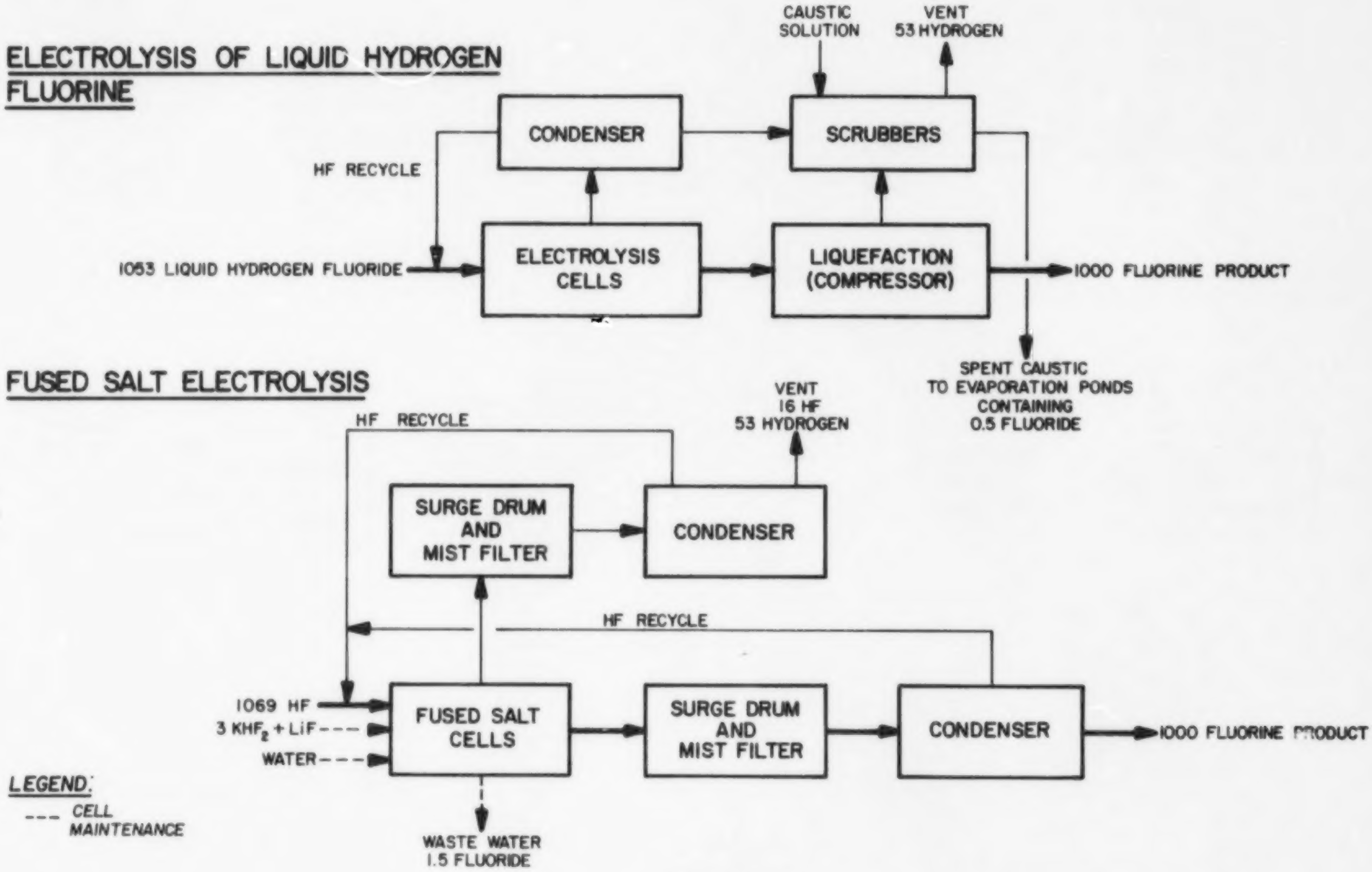


FIGURE 5-99
FLUORINE MANUFACTURE

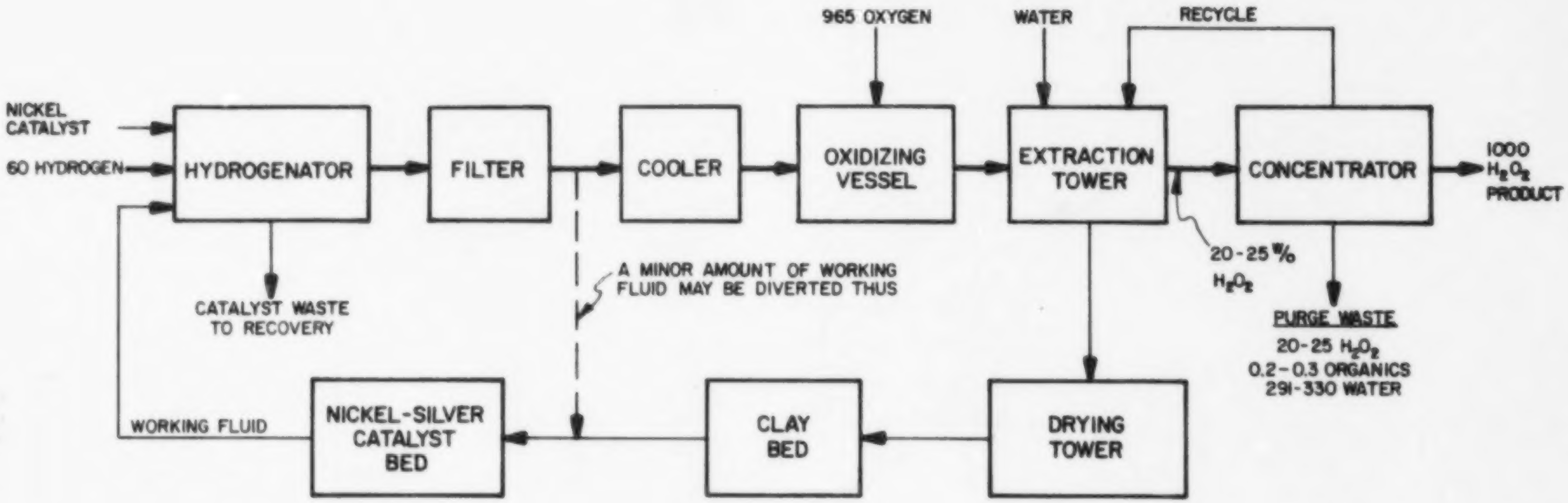


FIGURE 5-100
HYDROGEN PEROXIDE MANUFACTURE
BY THE RIEDL-PFLEIDERER PROCESS

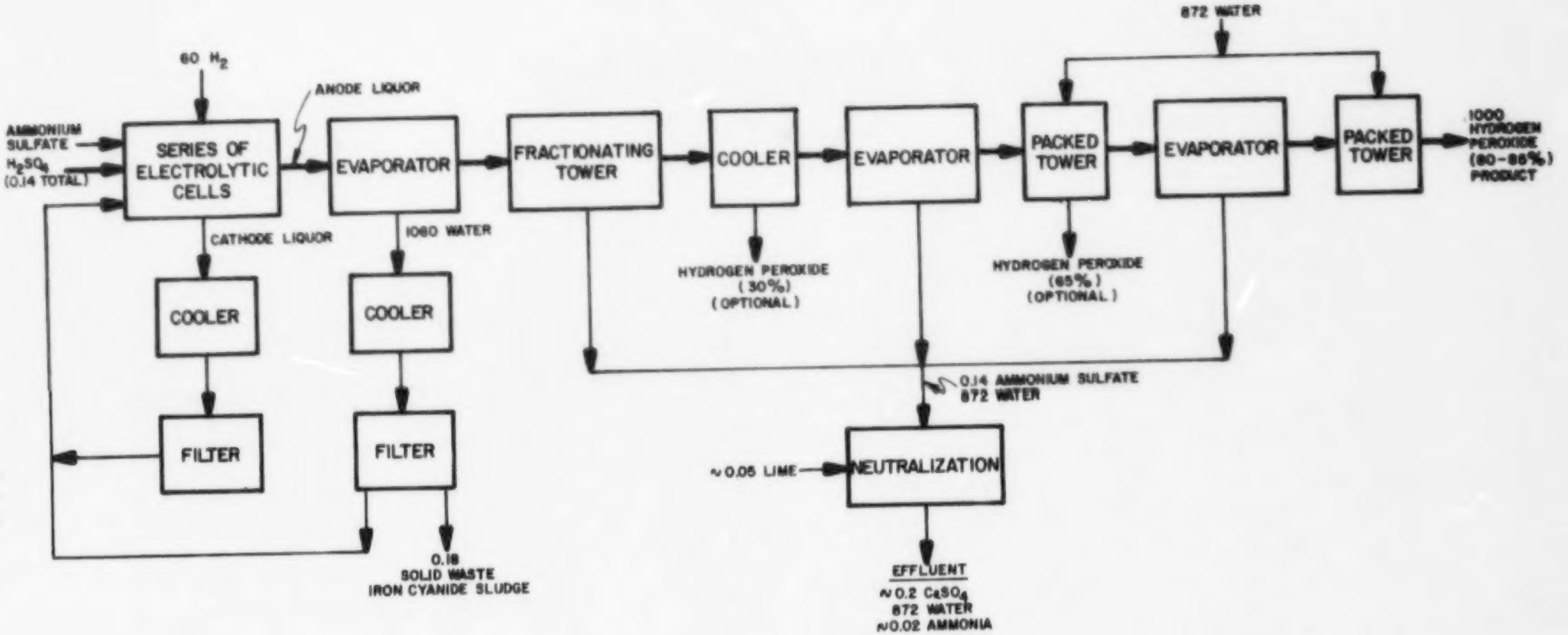


FIGURE 5-101
HYDROGEN PEROXIDE MANUFACTURE
BY THE ELECTROLYTIC PROCESS

5.5.7.16 Hypophosphites

Hypophosphorous acid and its salts are derived from treatment of elemental phosphorous with a boiling slurry of lime. In addition to calcium hypophosphite (which remains in solution) insoluble calcium phosphate is formed along with phosphine (PH_3) and hydrogen. The reactions which occur are highly complex. The excess calcium hydroxide is precipitated as carbonate and filtered from the solution. The solutions are evaporated to give a calcium hypophosphite intermediate product which is generally redissolved in water and reacted with sodium sulfate to yield a solution of the desired sodium salt. This solution is filtered to remove the calcium sulfate co-product and evaporated. According to the manufacturers contacted, the wastes from these processes consist of the following:

(a) Calcium sulfate from the conversion of the calcium salt. This is non-hazardous.
(b) Calcium carbonate from the lime removal step. This also is non-hazardous.
(c) A calcium phosphite mud consisting of about 92 percent (dry basis) $CaHPO_3.2H_2O$, with lesser amounts of other phosphite salts present. This mud is the principal waste-being generated in amounts of about 2.5-3 tons per ton of product. This waste is not considered to be hazardous.
(d) A gaseous waste containing hydrogen and phosphine. Combustion of this gas stream yields a gas containing phosphoric acid vapors which must be removed by wet scrubbing prior to venting to the atmosphere. Chemical treatment of this water-borne waste with lime yields calcium phosphate as another non-hazardous solid waste.

5.5.7.17 Iron Compounds

Ferric chloride is made by the reaction of iron, spent pickle liquor and chlorine. For technical solution grade product there are no wastes. For higher product grades, there are sludges produced from filtrations. However, these consist of iron and iron oxide and are not hazardous. The flow diagram is shown in Figure 5-102.

As shown in Figure 5-103, ferrous sulfate is recovered as a co-product of sulfate process titanium dioxide production. All wastes are associated with the TiO_2 production, which was discussed with SIC 2816.

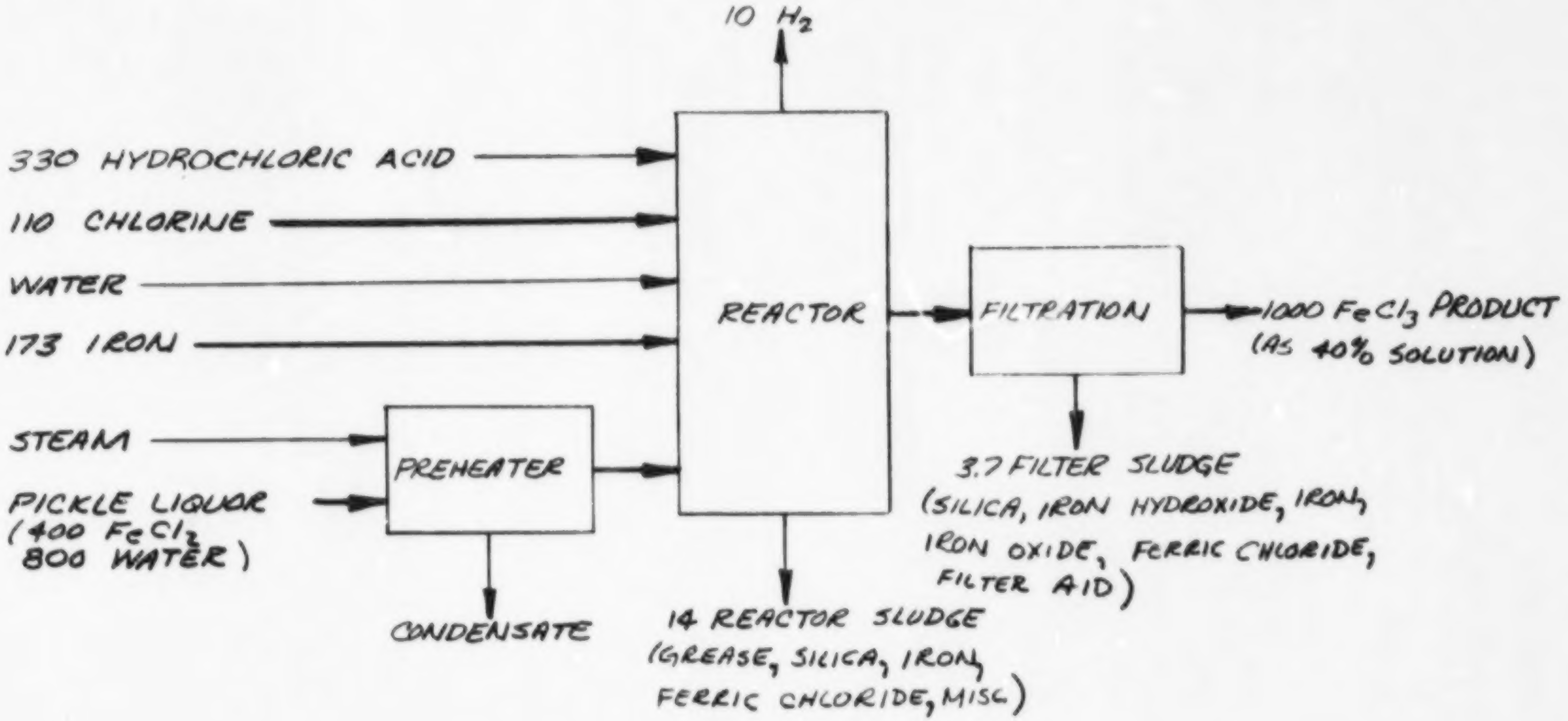

10 H_2
330 HYDROCHLORIC ACID
110 CHLORINE
WATER
173 IRON
STEAM
PICKLE LIQUOR (400 $FeCl_2$ 800 WATER)
PREHEATER
CONDENSATE
REACTOR
14 REACTOR SLUDGE (GREASE, SILICA, IRON, FERRIC CHLORIDE, MISC)
FILTRATION
3.7 FILTER SLUDGE (SILICA, IRON HYDROXIDE, IRON, IRON OXIDE, FERRIC CHLORIDE, FILTER AID)
1000 $FeCl_3$ PRODUCT (AS 40% SOLUTION)

FIGURE 5-102
FERRIC CHLORIDE MANUFACTURE
SOLUTION GRADE

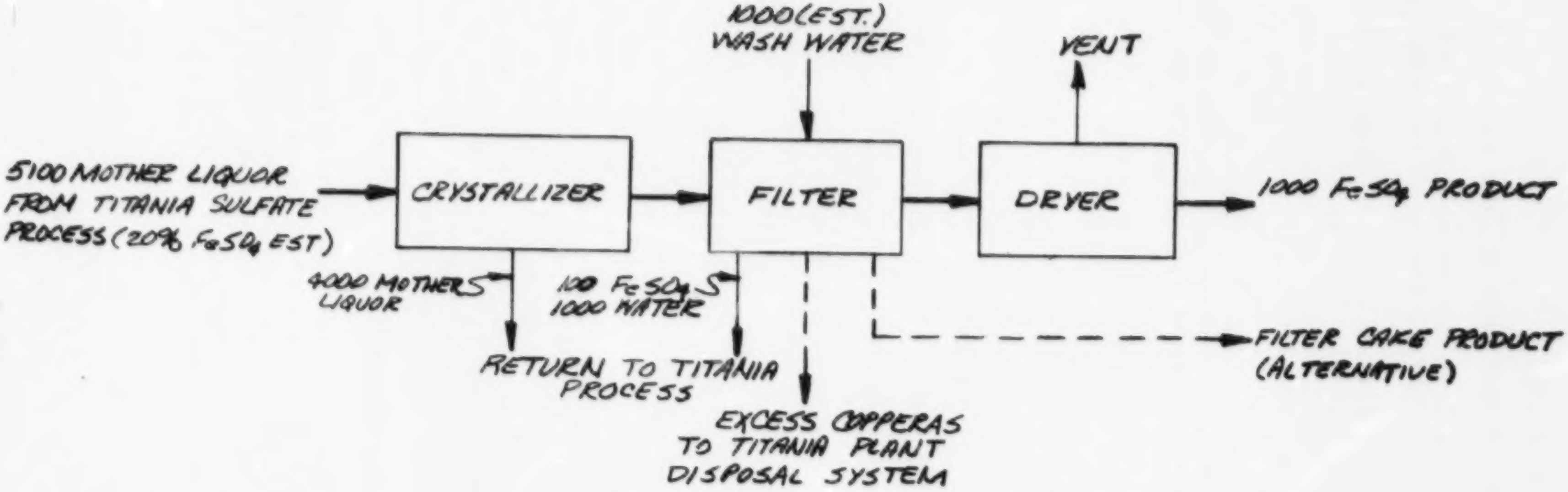

5100 MOTHER LIQUOR FROM TITANIA SULFATE PROCESS (20% $FeSO_4$ EST)
CRYSTALLIZER
4000 MOTHERS LIQUOR
RETURN TO TITANIA PROCESS
1000 (EST.) WASH WATER
FILTER
100 $FeSO_4$
1000 WATER
EXCESS COPPERAS TO TITANIA PLANT DISPOSAL SYSTEM
VENT
DRYER
1000 $FeSO_4$ PRODUCT
FILTER CAKE PRODUCT (ALTERNATIVE)

FIGURE 5-103
FERROUS SULFATE MANUFACTURE
FROM TITANIA SULFATE PROCESS WASTES

5.5.7.18 Lead Compounds (Other Than Pigments)

The manufacture of lead oxides was described earlier in the pigments section. Lead silicate is produced by two methods:

(a) Reaction of sodium silicate in excess in aqueous solution with soluble lead salts. Here, the product is recovered by filtration and all wastes are water-borne. Due to the extreme insolubility of lead silicate, water-borne wastes contain only trace amounts of lead.
(b) Thermal reaction of lead oxide and silica in a furnace process. Here all wastes are air-borne and consist of dusts which are recycled to the process.

Lead nitrate is manufactured principally from scrap lead battery plates as shown in Figure 5-104. Lead and antimony residues are disposed of as a by-product. No hazardous wastes destined for land disposal are generated by this process due to recovery of residues and by-products.

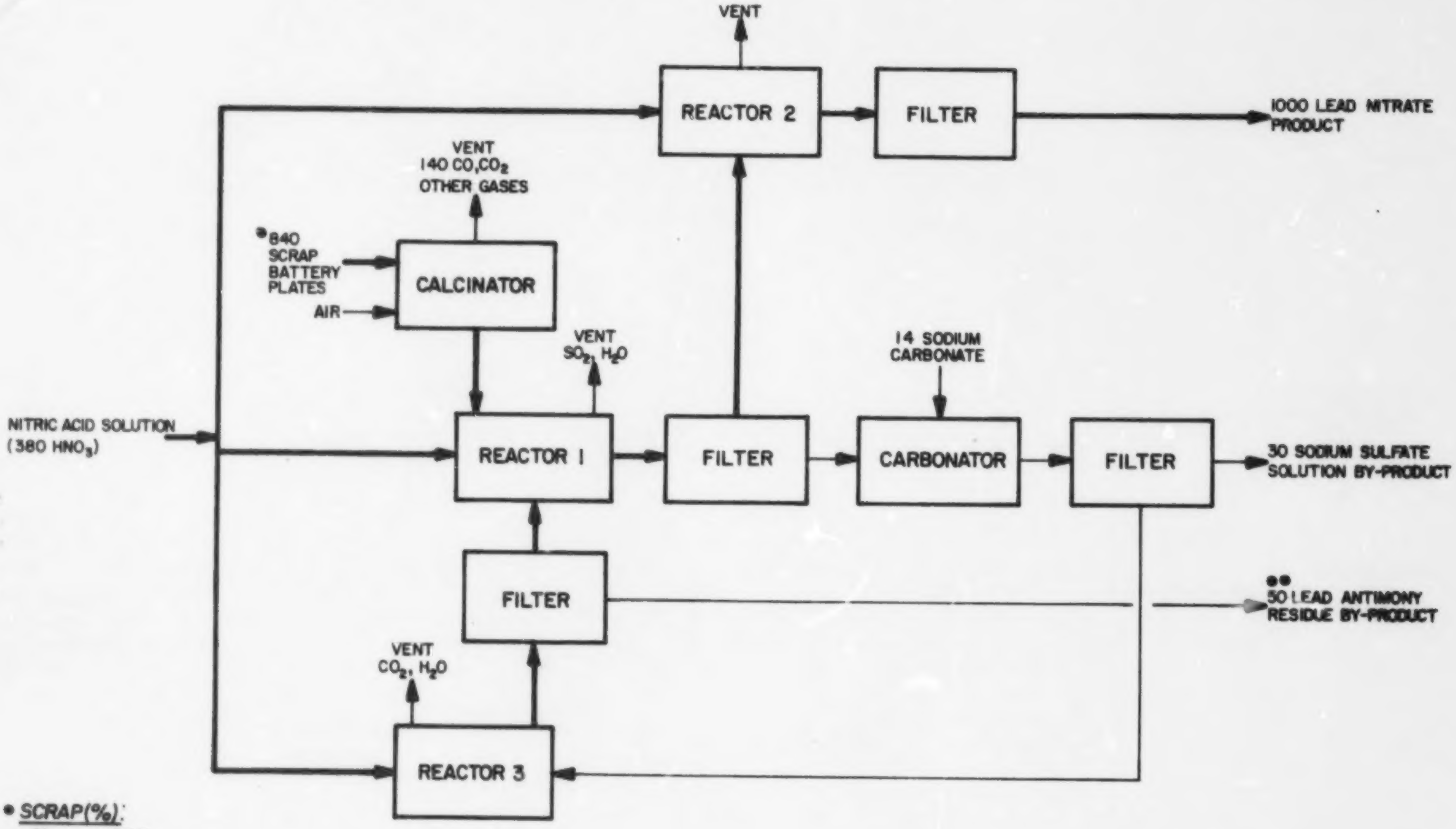
5.5.7.19 Lithium Compounds

Lithium compounds are produced by two methods:

(a) Extraction from brines. A number of materials are recovered from Searles Lake brines by a series of evaporation and recovery processes. Among these are a lithium phosphate which is converted to $LiCO_3$ for sale. All of the wastes from these operations (consisting largely of unrecovered salts) are returned to the brine source. There are no hazardous wastes; all wastes are recycled.
(b) By recovery from Spodumene Ore as shown in Figure 5-105 and 5-106. The ore is first roasted and then leached with sulfuric acid to recover lithium sulfate. This is then converted to $LiCO_3$ by reaction with soda ash. Sodium sulfate is recovered as a co-product. The $LiCO_3$ is then converted to other lithium salts by reaction with the appropriate mineral acids. The wastes from these processes consist of ore gangues (which are non-hazardous) and water-borne wastes containing alkali and alkaline earth sulfates. These also are not hazardous.

5.5.7.20 Magnesium Compounds

Magnesium carbonate is produced from dolomitic limestone by the following process: dolomite is calcined to yield a mixture of lime and MgO. This mixed material is then reacted with water and CO_2 to yield an aqueous solution of magnesium bicarbonate and a solid calcium carbonate phase. The calcium carbonate is then removed by filtration and dis-



• *SCRAP(%)*:

Pb	55.5
Sb	2.7
Sn	0.16
As	0.09
PbO	16.1
$PbSO_4$	9.8
PLASTIC	15.6

FIGURE 5-104
LEAD NITRATE MANUFACTURE

•• *RESIDUE(%)*:

Sb	44.8
Sn	2.7
As	1.5
$PbSO_4$	9.7
Pb	41.4

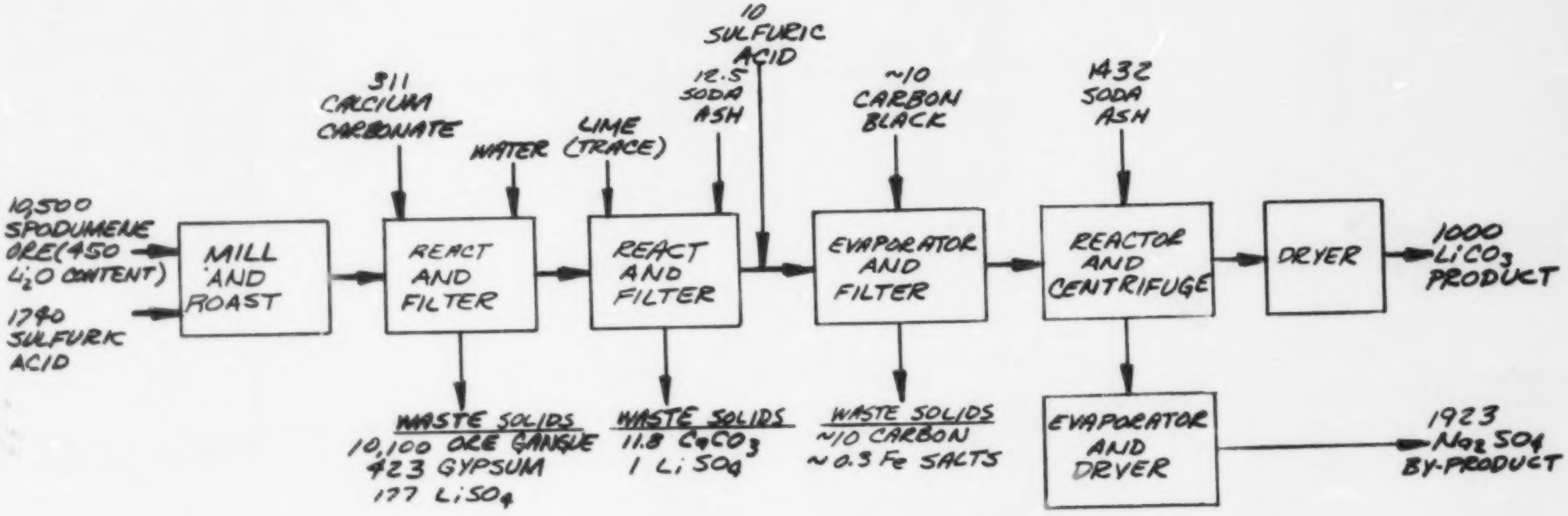


FIGURE 5-105

LITHIUM CARBONATE MANUFACTURE

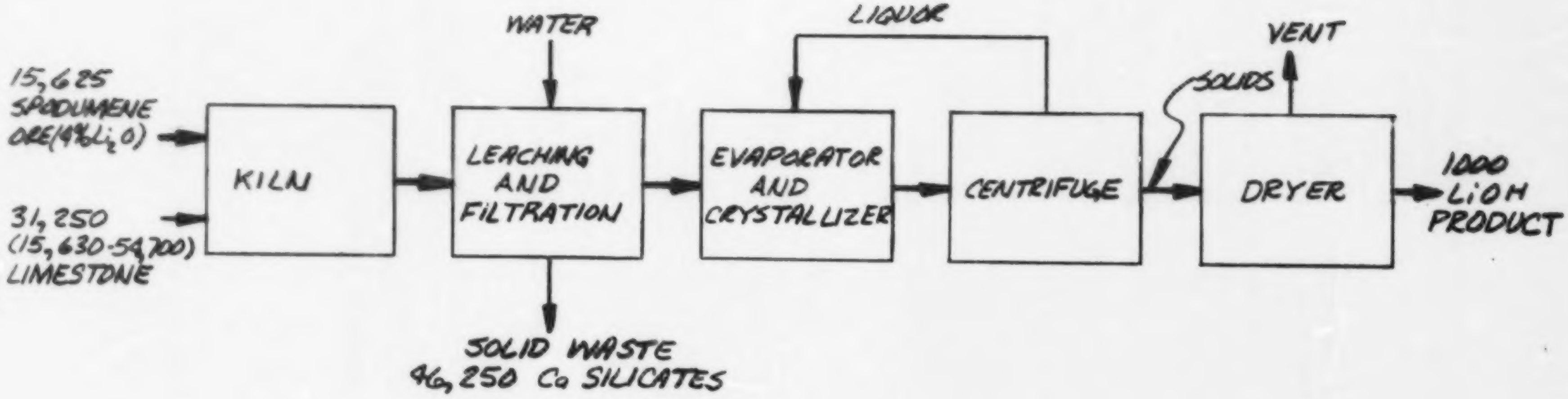


FIGURE 5-106
LITHIUM HYDROXIDE MANUFACTURE

carded as a non-hazardous solid waste. The magnesium bicarbonate solutions are then boiled to convert the bicarbonate to carbonate which is then recovered by filtration.

Magnesium oxide is produced by calcination of the pure carbonate. No hazardous solid wastes are produced here.

As shown in Figure 5-107, magnesium sulfate is produced by reaction of the oxide or carbonate with sulfuric acid. The product is then recovered by evaporation.

Magnesium chloride is produced by two methods:

(a) As a co-product of K_2SO_4 manufacture from langbeinite ore or from K_2SO_4 recovery operations at Great Salt Lake. In these cases, no hazardous wastes are produced.

(b) By recovery from sea water. Here, sea water is first treated with lime to effect precipitation of magnesium hydroxide. This material is recovered by filtration and then reacted with HCl to yield a hydrated magnesium chloride. The hydrated material is then heated in an HCl atmosphere to yield an anhydrous product. From these operations all wastes are water-borne and non-hazardous after treatment.

5.5.7.21 Manganese Compounds

As shown in Figure 5-108, manganese sulfate is produced as a co-product in hydroquinine manufacture which involves the oxidation of aniline with manganese dioxide (present as pyrolucite manganese ore) and sulfuric acid. All of the wastes from the process are water-borne and, while wastewater treatment does generate some solids, these are not hazardous. In addition, they are principally attributable to hydroquinone manufacture which is not an SIC 281 product operation.

Manganese dioxide is produced by oxidation of manganous salts. The product is separated by filtration and there are no hazardous wastes produced.

5.5.7.22 Mercury (Redistilled)

Redistilled mercury is obtained by the redistillation of mercury initially produced by retorting cinnabar ore. In this process, there are small amounts of solid waste (metal impurities in the crude mercury) which are recovered from the stills. These materials are generally recovered and reprocessed for their precious metal values.

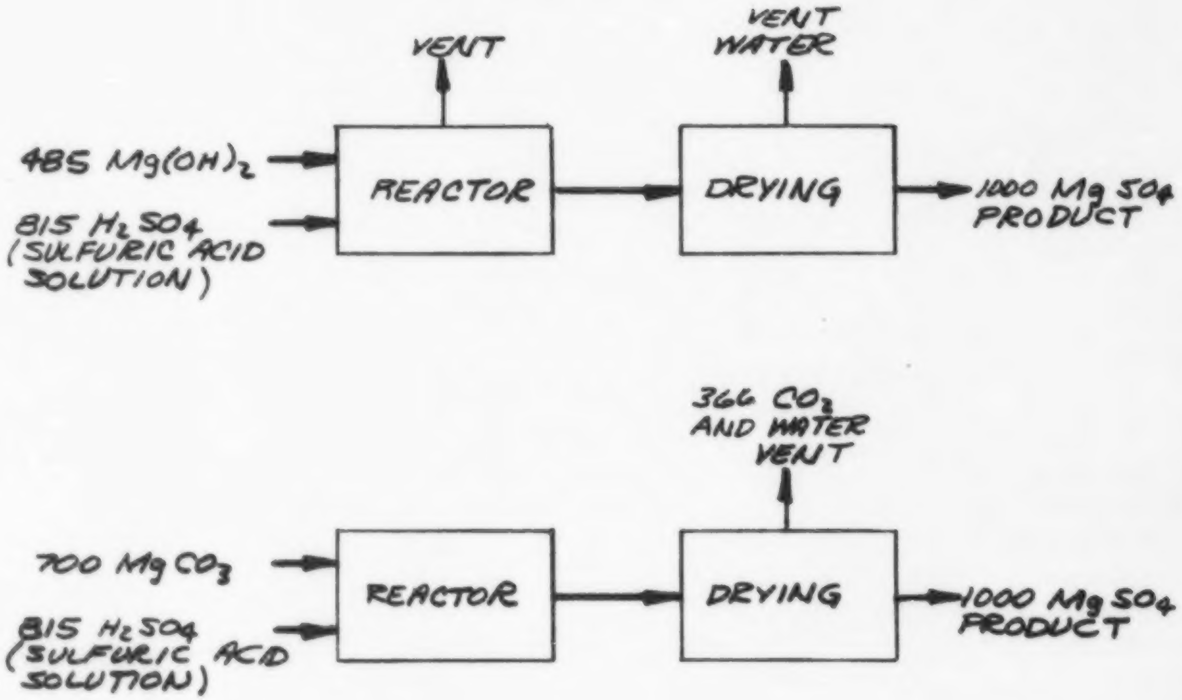


FIGURE 5-107
MAGNESIUM SULFATE MANUFACTURE

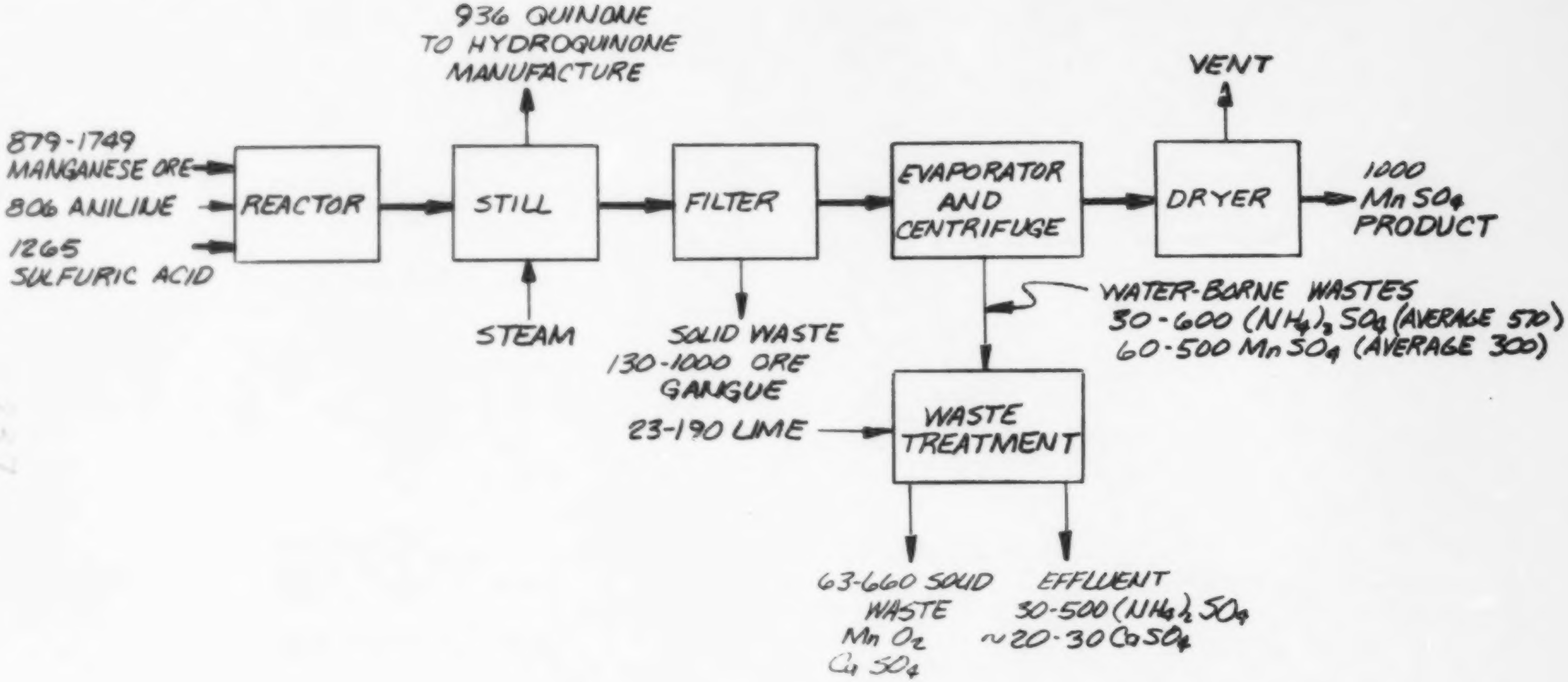

879-1749 MANGANESE ORE
806 ANILINE
1265 SULFURIC ACID
REACTOR
936 QUINONE TO HYDROQUINONE MANUFACTURE
STILL
STEAM
FILTER
SOLID WASTE 130-1000 ORE GANGUE
EVAPORATOR AND CENTRIFUGE
VENT
DRYER
1000 MnSO4 PRODUCT
WATER-BORNE WASTES
30-600 (NH4)2SO4 (AVERAGE 570)
60-500 MnSO4 (AVERAGE 300)
23-190 LIME
WASTE TREATMENT
63-660 SOLID WASTE MnO2 CaSO4
EFFLUENT 30-500 (NH4)2SO4 ~20-30 CaSO4

FIGURE 5-108

MANGANESE SULFATE MANUFACTURE

5.5.7.23 Mercury Compounds

Mercury oxides are made by three processes , each of which generate some mercury bearing wastes that are recycled. These processes are shown in Figures 5-109 and 5-110. The mercury sulfide from waste water treatment is relatively pure and it is recovered for the mercury present and not disposed of as a waste.

The first process involves reaction of mercuric chloride with caustic soda in aqueous solution. The product yellow mercury oxide, is recovered by filtration, washed, calcined and dried. Treatment of the wastewaters with sulfide produces some mercury sulfide as a solid waste, which is recycled.

The latter two processes produce the red oxide of mercury. In the second, mercurous nitrate is calcined to give the oxide. Nitrogen dioxide gas is formed as the co-product. Scrubbing of vent gases with alkaline solutions generates a wastewater stream which contains minor amounts of mercury compounds. Sulfide treatment of this stream will also produce minor amounts of HgS, which is recycled.

In the third process, mercuric chloride and soda ash are reacted in hot aqueous solution. The product precipitates and CO_2 is liberated as a gaseous co-product. The mercury oxide is then recovered by filtration, washed, and dried. The wastewater here is also treated to remove mercury as the sulfide, which is recycled.

Calomel (mercurous chloride) is produced by reaction of mercury with chlorine, as shown in Figure 5-111. The product is thoroughly washed to dissolve any bichloride formed along with the calomel, and is then dried and packaged. There are two sources of waste:

(a) Scrubbing of the vent gases from the reactor produces a water-borne waste which may contain mercury salts. Treatment of this waste stream will effect precipitation of a very small amount of mercury sulfide which will be a solid waste that is recycled.

(b) The washwaters used to remove bichloride of mercury from the product contain considerable amounts of this material. These are not wasted but are evaporated to recover a co-product, as is shown.

Bichloride of mercury ($HgCl_2$) is produced by reaction of mercury with excess chlorine. The product is recovered as a solid and packaged. The only wastes arise from scrubbing of

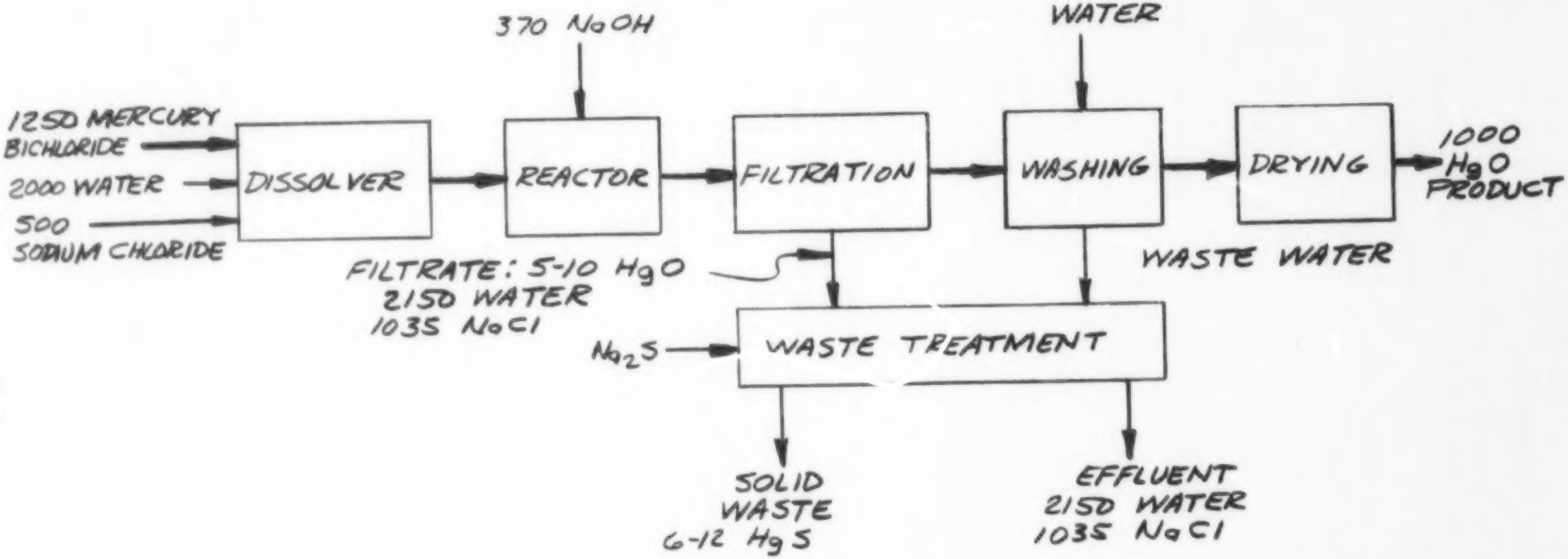


FIGURE 5-109
YELLOW MERCURIC OXIDE MANUFACTURE

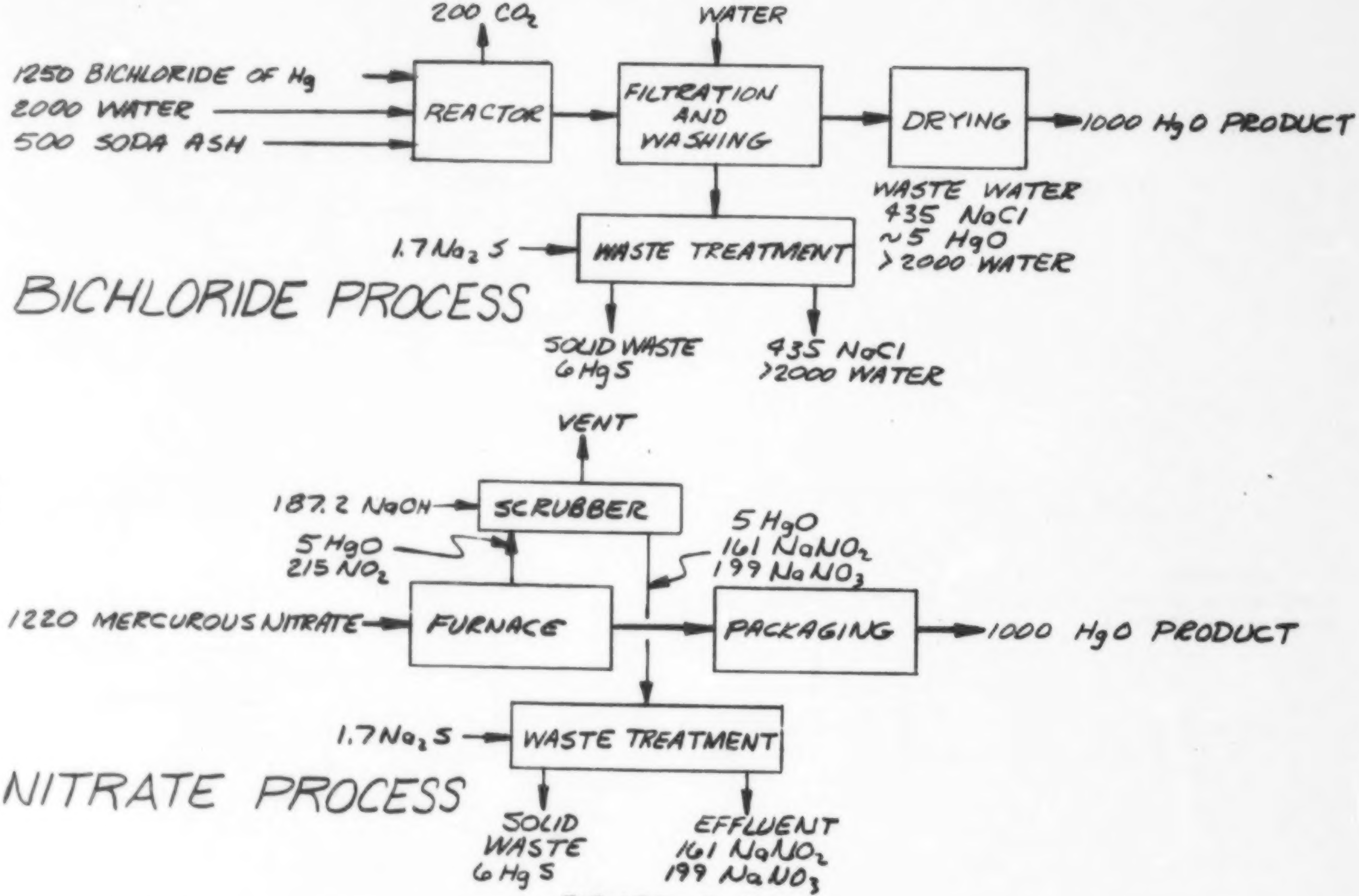
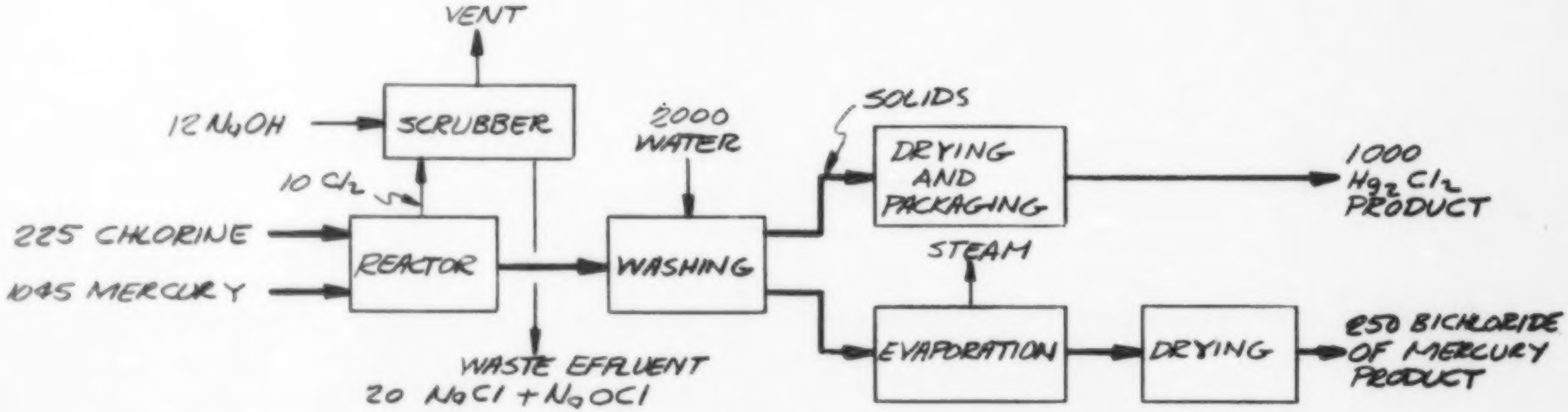


FIGURE 5-110

RED MERCURIC OXIDE MANUFACTURE



MERCUROUS CHLORIDE MANUFACTURE

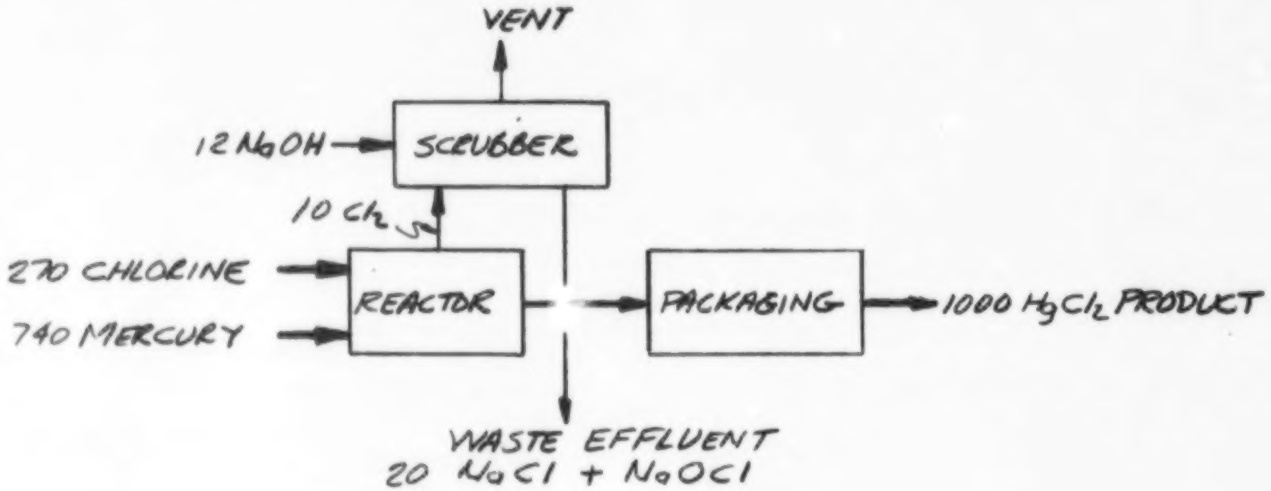


FIGURE 5-111
BICHLORIDE OF MERCURY MANUFACTURE

the gaseous effluent. This yields a wastewater from which a very small amount of mercury is removed by sulfide precipitation, which is recycled.

The major constituent of solid wastes from all these process wastewaters is HgS. The concentration is such that the overall properties of the waste are the same as those described for pure HgS (Appendix A). Stringent safeguards to protect against environmental contamination are required. No instance was found in which these wastes were not recycled rather than land disposed.

5.5.7.24 Nickel Compounds

Nickel sulfate is made by reaction of nickel oxide with sulfuric acid as shown in Figure 5-112. In some cases, the oxide is generated on-site by treatment of spent nickel plating solutions. Solid wastes are produced from filtration of product solutions prior to evaporation. The amounts of these solids are small and they are usually reprocessed to reclaim nickel values. There are also small amounts of solids generated by wastewater treatments. However, these materials (nickel oxides) are generated in very small quantities at only a few locations.

Nickel hydroxide and nickel hydroxide wastes are not as severely hazardous as cadmium, mercury, chromium, etc.; however, it is not an inert material (e.g., silica) or a generally non-hazardous material (e.g., calcium sulfate or sodium chloride). $Ni(OH)_2$ is a borderline material between severely hazardous and moderately hazardous materials. Its properties are described in Appendix A; and safeguards to prevent migration of the waste from land disposal sites are required.

Nickel ammonium sulfate is prepared by evaporation of aqueous solutions to which the two sulfates have been added. There are no land destined wastes produced here.

Nickel carbonate is produced by reaction of a soluble nickel salt (i.e. $NiSO_4$) in water with soda ash. The insoluble product is recovered by filtration. No land destined wastes are produced.

5.5.7.25 Phosphorus

This material is produced as shown in Figure 5-113 with minor variations by thermal reaction of coke, silica, and phosphate rock. The product P_4 distills from the mixture and is collected in water. There are several possibly hazardous wastes involved:

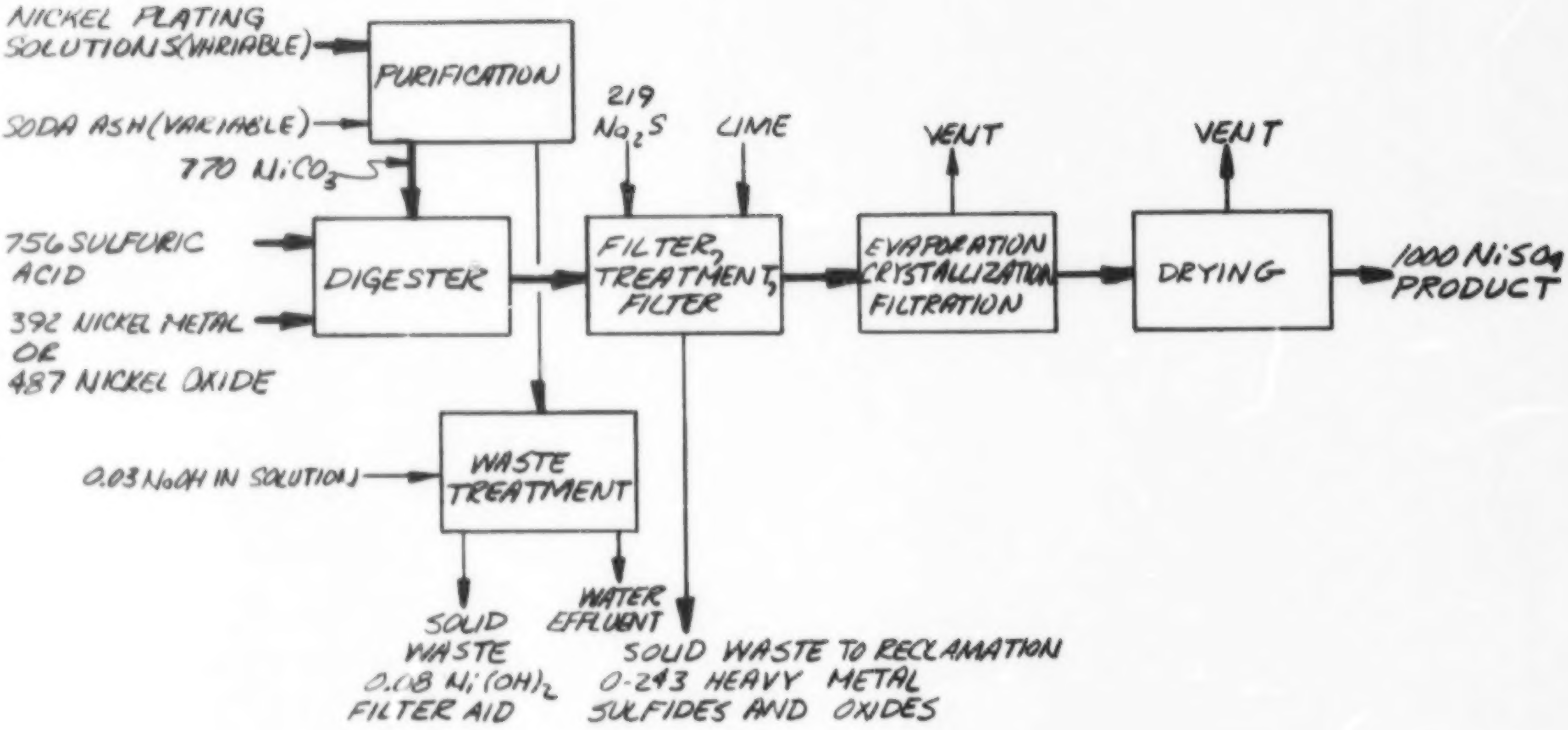

NICKEL PLATING SOLUTIONS(VARIABLE)
SODA ASH(VARIABLE)
770 NiCO3
756 SULFURIC ACID
392 NICKEL METAL OR 487 NICKEL OXIDE
PURIFICATION
DIGESTER
219 Na2S
LIME
FILTER, TREATMENT, FILTER
VENT
EVAPORATION CRYSTALLIZATION FILTRATION
VENT
DRYING
1000 NiSO4 PRODUCT
0.03 NaOH IN SOLUTION
WASTE TREATMENT
SOLID WASTE 0.08 Ni(OH)2 FILTER AID
WATER EFFLUENT
SOLID WASTE TO RECLAMATION 0.243 HEAVY METAL SULFIDES AND OXIDES

FIGURE 5-112
NICKEL SULFATE MANUFACTURE

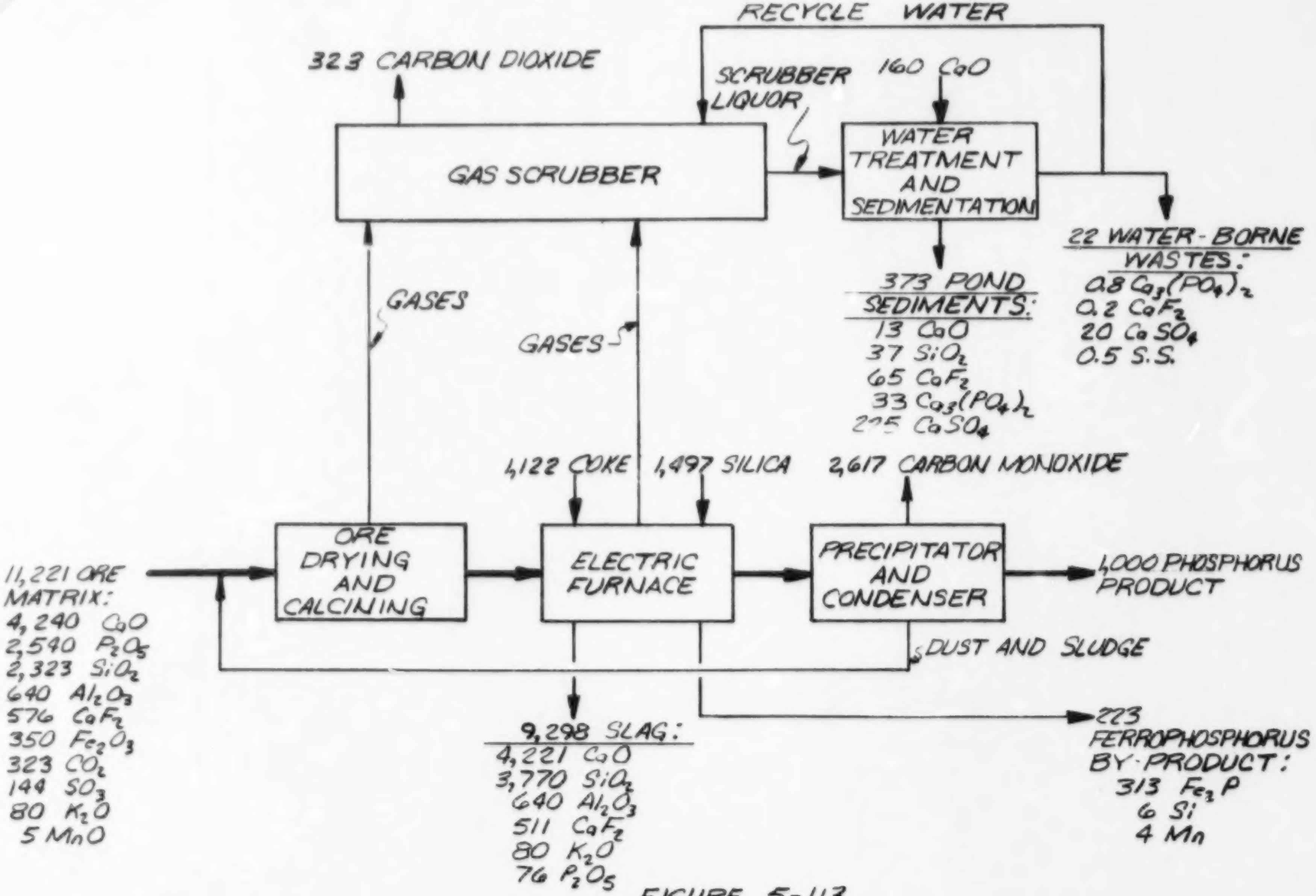


FIGURE 5-113
PHOSPHORUS MANUFACTURE

(a) The furnace slag and dusts collected from the process are usually wasted. These contain considerable amounts of fluorides as well as radioactive material such as uranium oxide. Leaching data from industry shows that the ceramic nature of phosphorus production furnace slag effectively binds the potentially hazardous constituents (fluorides and uranium oxide) so that migration of hazardous constituents from the waste does not occur upon land disposal, hence this is not hazardous.

(b) Waters containing unrecovered colloidal phosphorus are frequently treated to recover this material, some of which may not be suitable for use as product. The properties of colloidal phosphorus are discussed in Appendix A. Phosphorus containing wastewaters are hazardous to both plants and animals.

(c) Scrubber water treatment produces pond sediments containing calcium fluoride, other calcium salts including calcium phosphate, silicates, and variable amounts of colloidal phosphorus. Colloidal phosphorus and calcium fluoride are the potentially hazardous constituents. Calcium fluoride comprises roughly 10 percent of the total wastes (w/w dry basis) and colloidal phosphorus comprises 8 percent (w/w basis) or higher in some instances. The properties of both waste constituents are described in Appendix A. The concentration of these constituents in the waste is sufficient to require stringent safeguards upon land disposal.

5.5.7.26 Phosphorus Oxides, Sulfides, and Chlorides

As shown in Figure 5-114, phosphorus pentoxide is made by burning of phosphorus with oxygen followed by condensation of the formed product. Small amounts of calcium phosphate (which is not severely hazardous) are formed from wastewater treatment. Periodically there are minor amounts of phosphoric acid-contaminated brick to be disposed of.

As shown in Figure 5-115, phosphorus pentasulfide is made by reaction of phosphorus and sulfur. The wastes from reactor water seals, still residues, and dust collection equipment are arsenic sulfide, phosphorus, phosphorus trisulfude, phosphorus pentasulfide dust, glassy phosphates, iron sulfide, and carbon disulfide. This constitutes a hazardous waste stream. The properties are described in Appendix A. In addition to the potential environmental hazards, the reactivity of this waste necessitates special handling. The P_2S_5 waste constituent results from equipment cleanout.

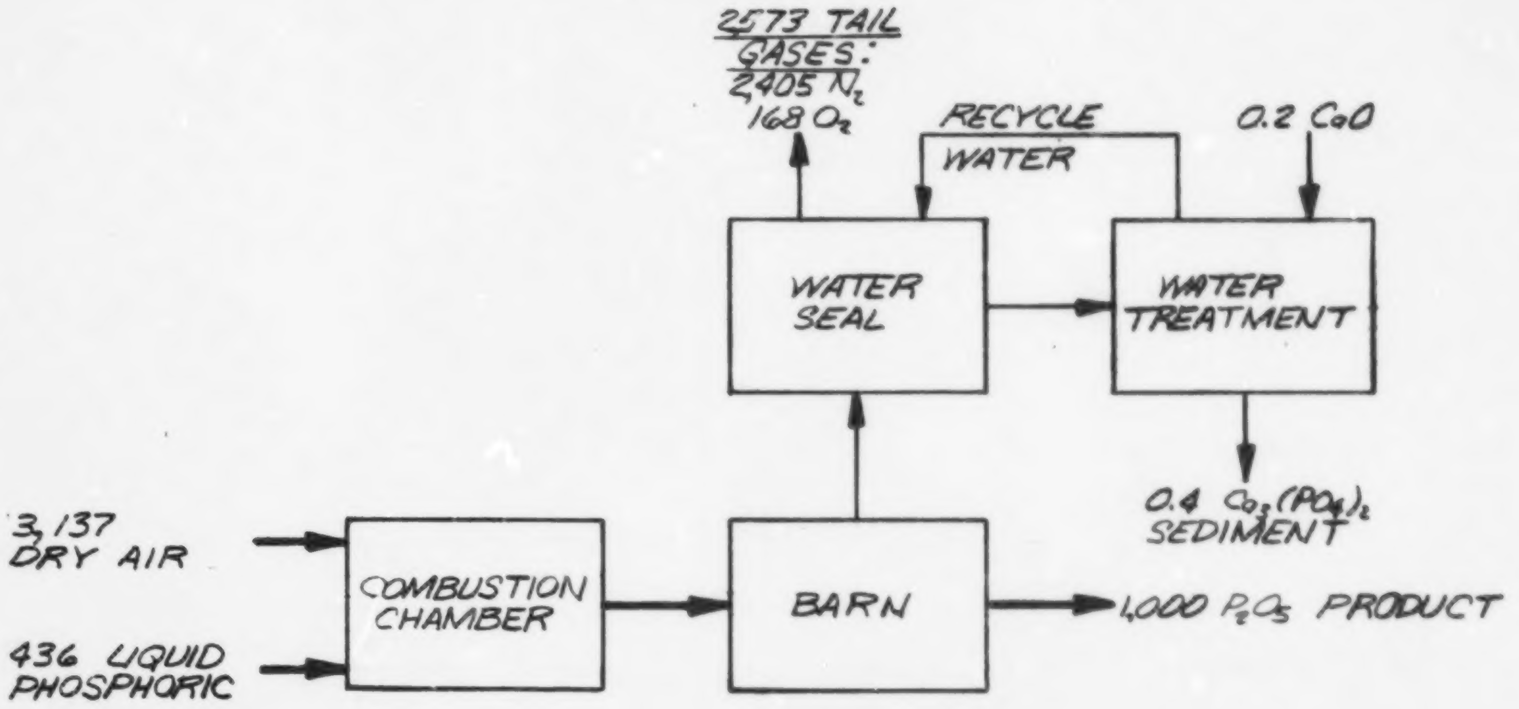


FIGURE 5-114
PHOSPHORUS PENTOXIDE MANUFACTURE

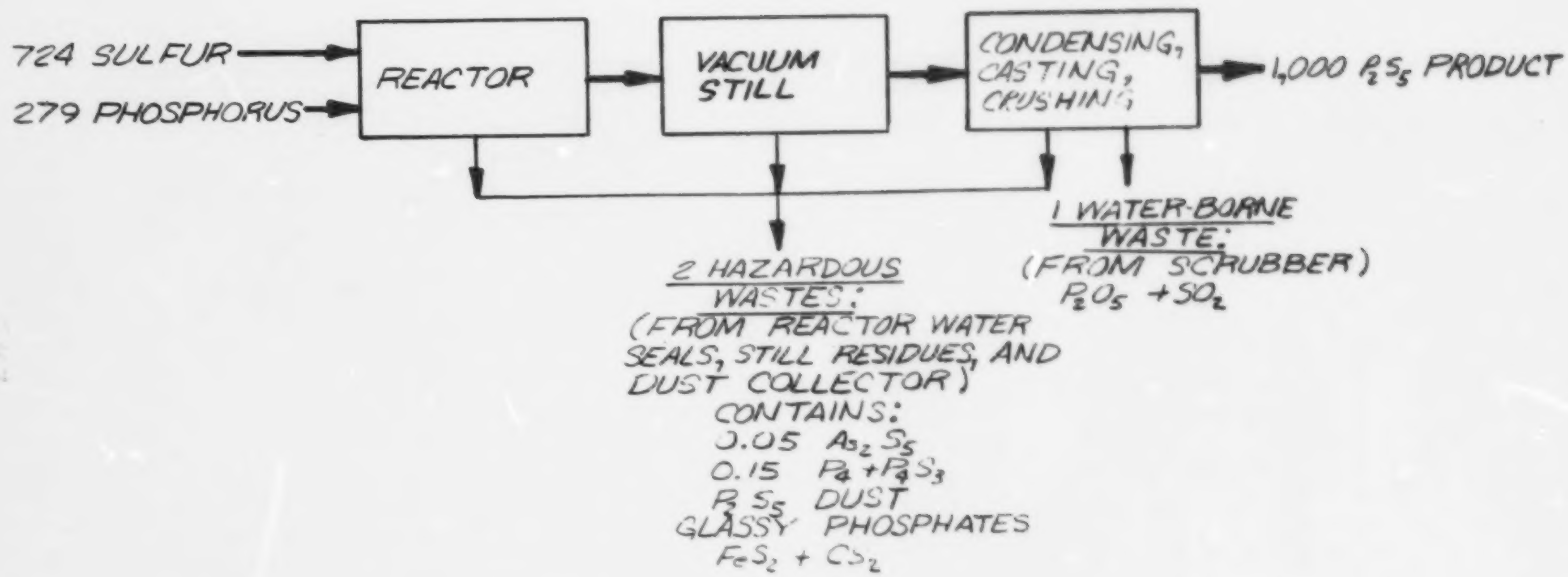


FIGURE 5-115
PHOSPHORUS PENTASULFIDE MANUFACTURE

As shown in Figure 5-116, phosphorus trichloride is made by reaction of phosphorus with chlorine. For the normal process there is no solid waste, but in the case of a high purity product, purification is achieved by fractional distillation which leaves behind small amounts of the hazardous waste, arsenic trichloride. Its properties are detailed in Appendix A.

As shown in Figure 5-117, phosphorus oxychloride is produced by reaction of PCl_3, P_2O_5, and chlorine, followed by fractional distillation to recover the desired product. No hazardous wastes are generated.

5.5.7.27 Potassium Permanganate

As shown in Figure 5-118, this compound is produced from manganese ore (MnO_2) by a rather complicated process involving oxidation of the manganese in the ore to manganate followed by electrochemical conversion to the permanganate. There are solid wastes generated in the form of ore residues, but these consist largely of insolubles such as silica and are non-hazardous.

5.5.7.28 Radioactive Chemicals

There are small amounts of a wide variety of isotope labelled compounds produced in the U. S. by a few manufacturers. The processes involved in these cases are the normal ones, except that isotopically pure starting materials are used. In cases where the isotopes in question are radioactive, regulations established by the AEC are followed in disposal of wastes. The amounts of these wastes are very minor.

5.5.7.29 Selenium and Tellurium

These products, along with tellurium dioxide are recovered from copper smelter flue dusts. The dusts are processed to recover copper and precious metal values and are then leached with alkaline solutions to dissolve the selenium and tellurium salts present. These solutions are then reacidified. Tellurium dioxide precipitates, with part being recovered for sale and the remainder treated with SO_2 to form selenium, which is recovered by filtration as a product.

The majority of the wastes from this process are water-borne. Most of the solids removed by the various filtration steps are reprocessed to recover metal values. The only hazardous materials which are not recycled are various wash and process waters which may contain traces of

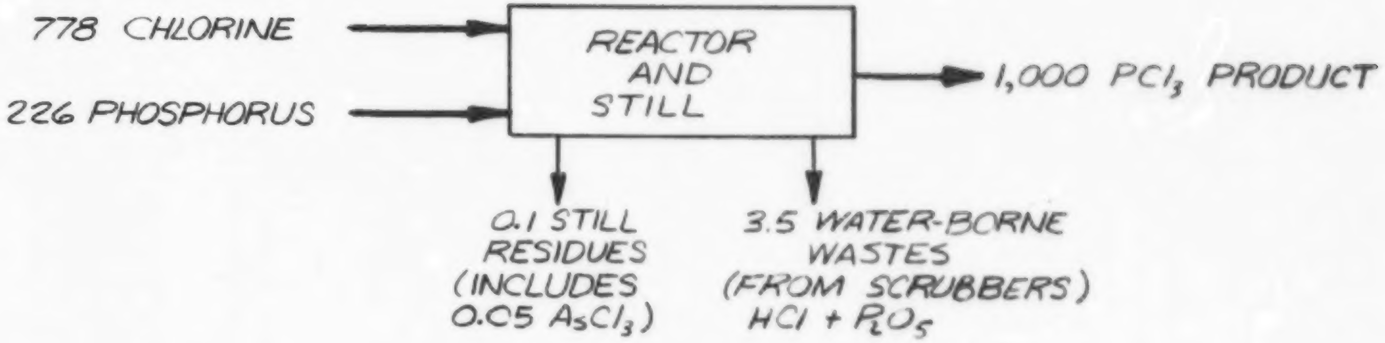

778 CHLORINE
226 PHOSPHORUS
REACTOR AND STILL
1,000 PCl_3 PRODUCT
0.1 STILL RESIDUES (INCLUDES 0.05 $AsCl_3$)
3.5 WATER-BORNE WASTES (FROM SCRUBBERS) $HCl + P_2O_5$

FIGURE 5-116

PHOSPHORUS TRICHLORIDE MANUFACTURE

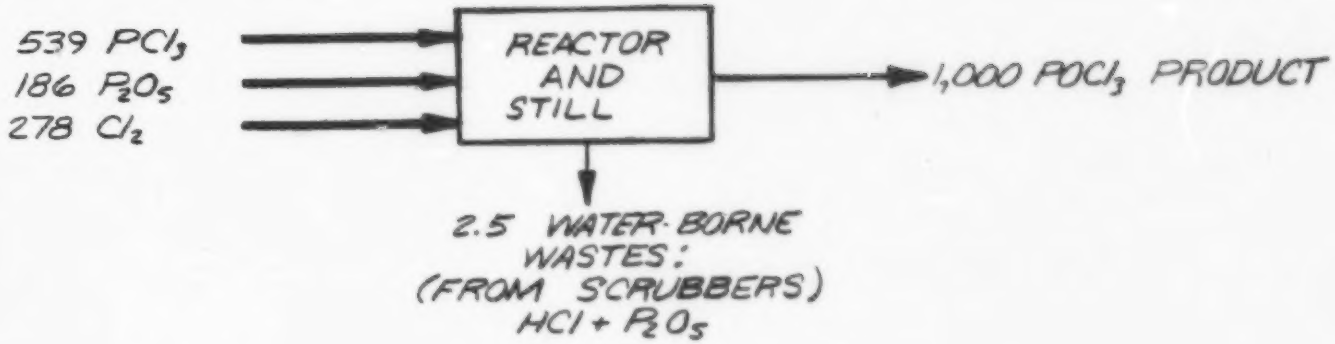


FIGURE 5-117
PHOSPHORUS OXYCHLORIDE MANUFACTURE

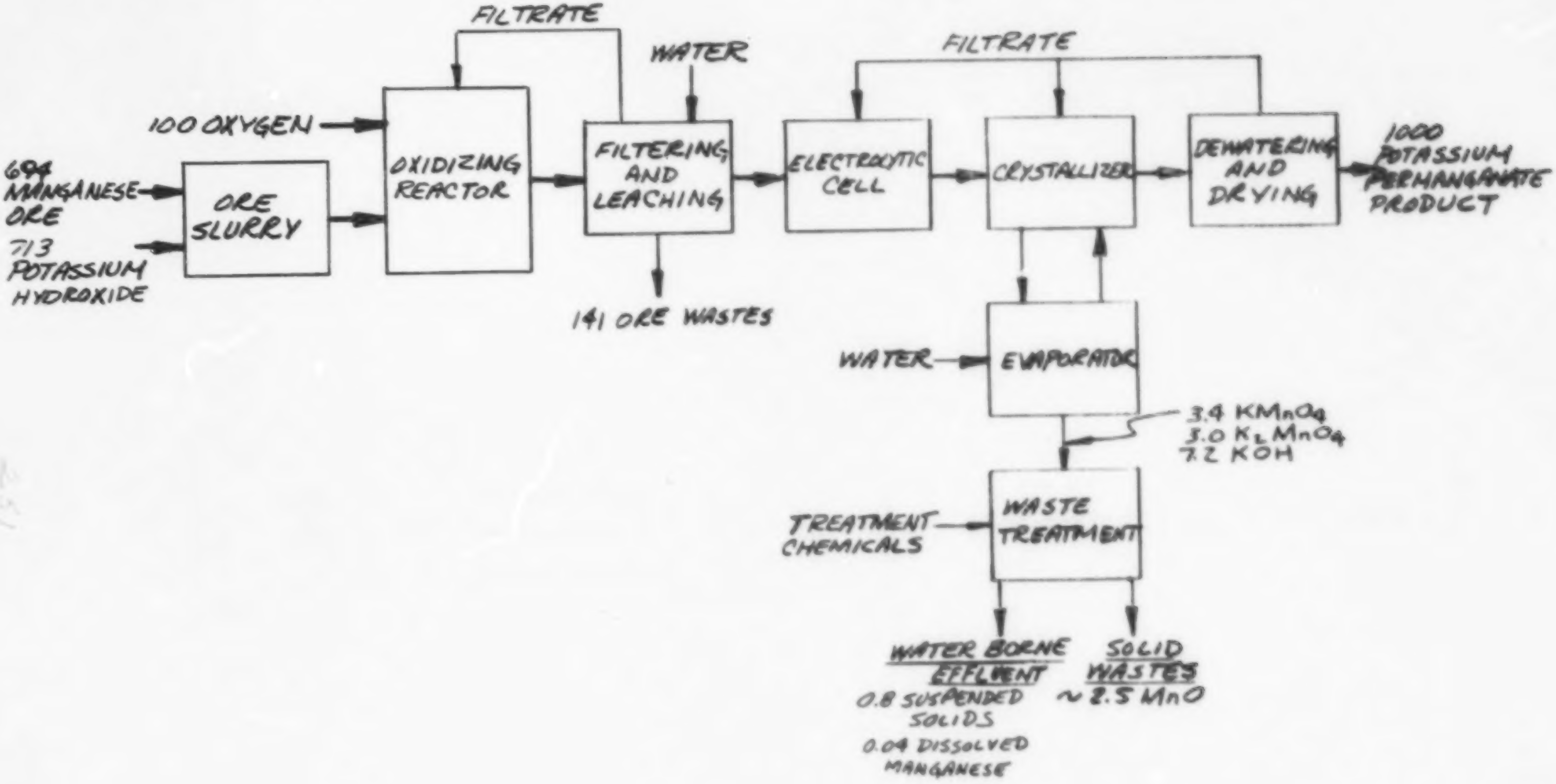


FIGURE 5-118

POTASSIUM PERMANGANATE MANUFACTURE

selenium. Chemical treatment of these with iron salts removes selenium as the insoluble selenide. Only four plants are involved, and the amounts of selenium-bearing wastes are very small and economically insignificant. The properties of selenium and selenides are discussed in Appendix A.

5.5.7.30 Silver Compounds

Silver nitrate, the only large volume silver compound production, is made by the reaction of silver with nitric acid. The process is shown in Figure 5-119. The only solid wastes generated are heavy metal-containing sludges from filtration steps and solids recovered from wastewater treatment which contain the following hazardous constituents: silver, mercury, cadmium, and lead. The properties of these are discussed in Appendix A. Due to the high cost of silver most of these materials are reprocessed and not discarded.

5.5.7.31 Strontium Compounds

Strontium compounds are made in a manner similar to that for barium compounds (discussed earlier) and in the same facilities. The flow diagram for strontium carbonate is shown in Figure 5-120. The barium sulfate and strontium sulfate containing wastes that are land disposed are not hazardous.

5.5.7.32 Sulfur Dioxide

This product is made by the burning of sulfur in air as shown in Figure 5-121. The combustion products are cooled, dried, and filtered, then compressed and cooled to liquefy the gas. No hazardous wastes are generated, and no wastes are disposed of on land.

5.5.7.33 Sulfur Chlorides (SCl_2 and S_2Cl_2)

As shown in Figure 5-122, these compounds are produced by reaction of sulfur and chlorine under controlled conditions. All of the wastes are due to the scrubbing of tail gases with alkaline waters and are non-hazardous.

Sulfur Oxychlorides

Thionyl chloride ($SOCl_2$) is made by two producers, each of which employs their own patented process. In the first, sulfur monochloride (S_2Cl_2) is reacted with chlorine and sulfur trioxide in the liquid phase in the presence of an antimony trichloride catalyst under pressure. The thionyl chloride is then separated by distillation from the catalyst

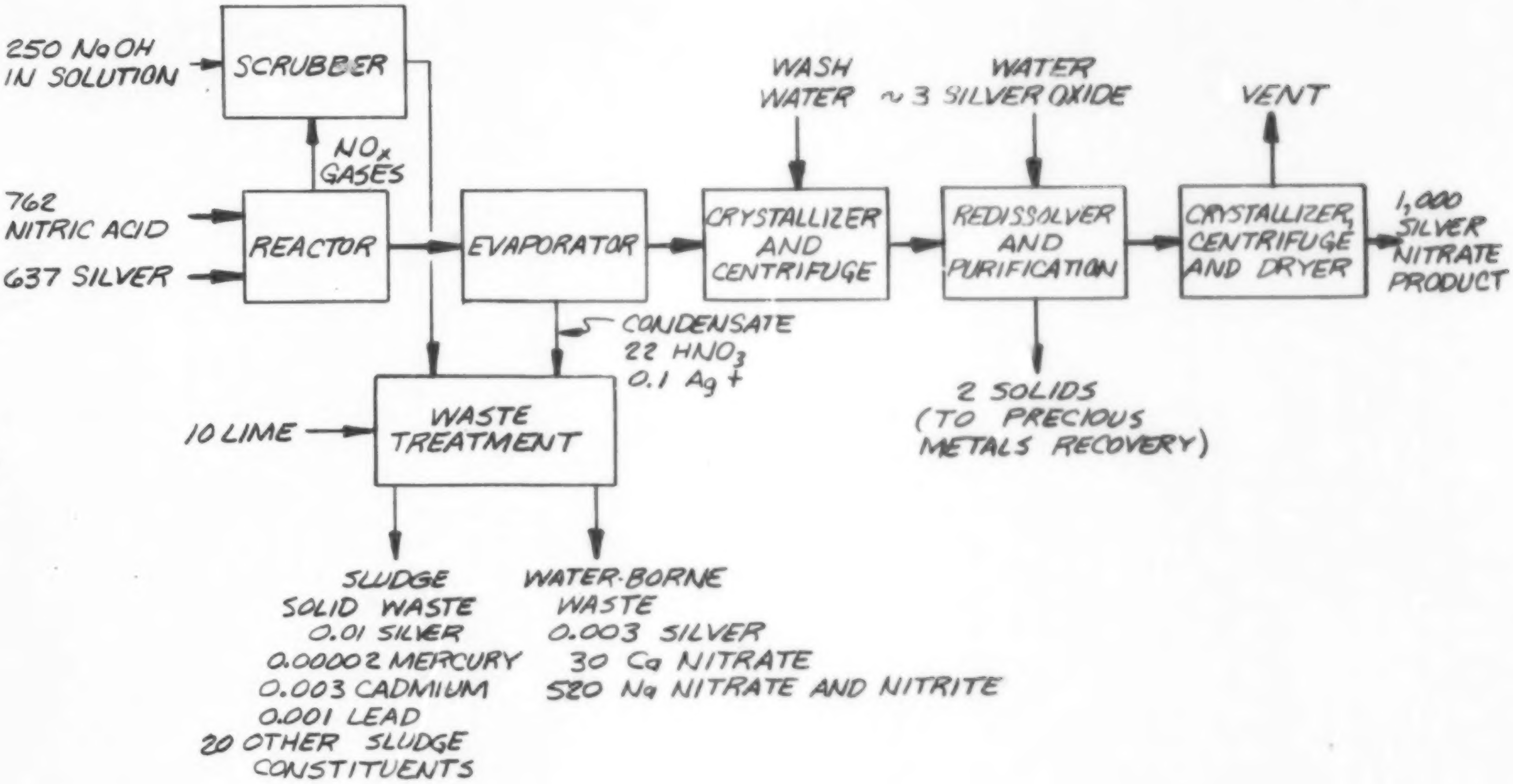


FIGURE 5-119

SILVER NITRATE MANUFACTURE

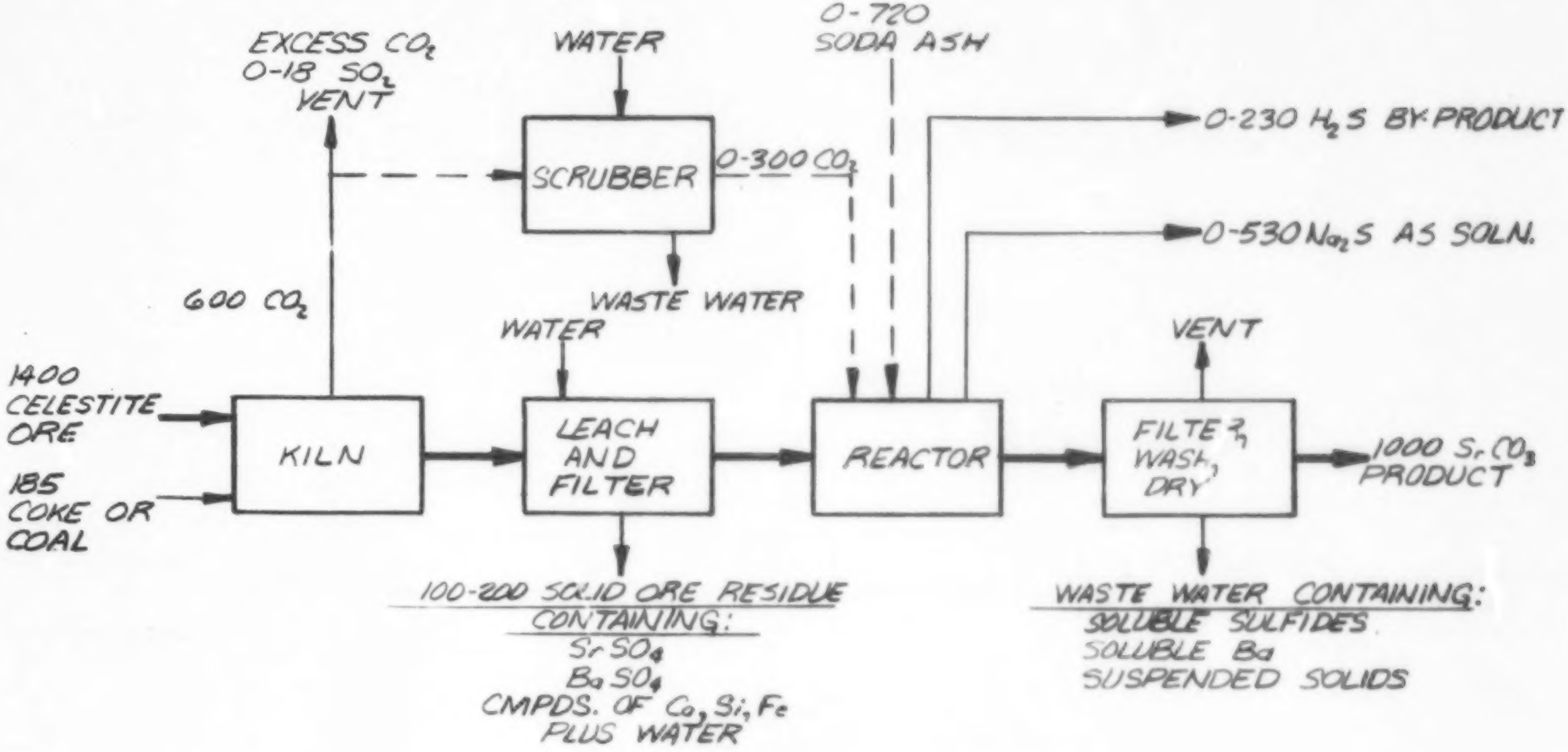


FIGURE 5-120
STRONTIUM CARBONATE MANUFACTURE

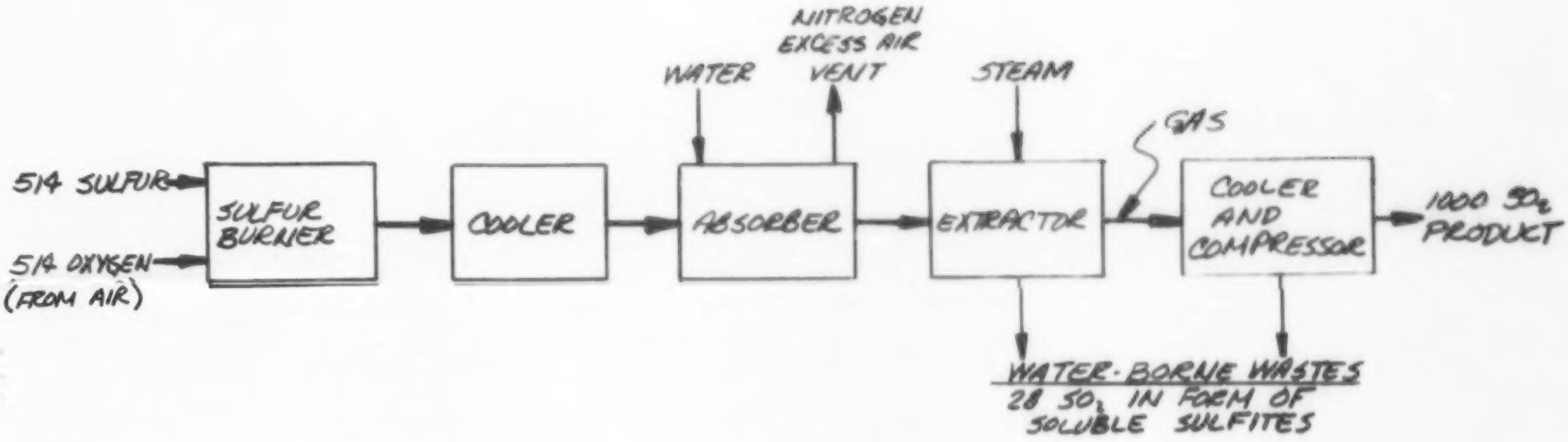
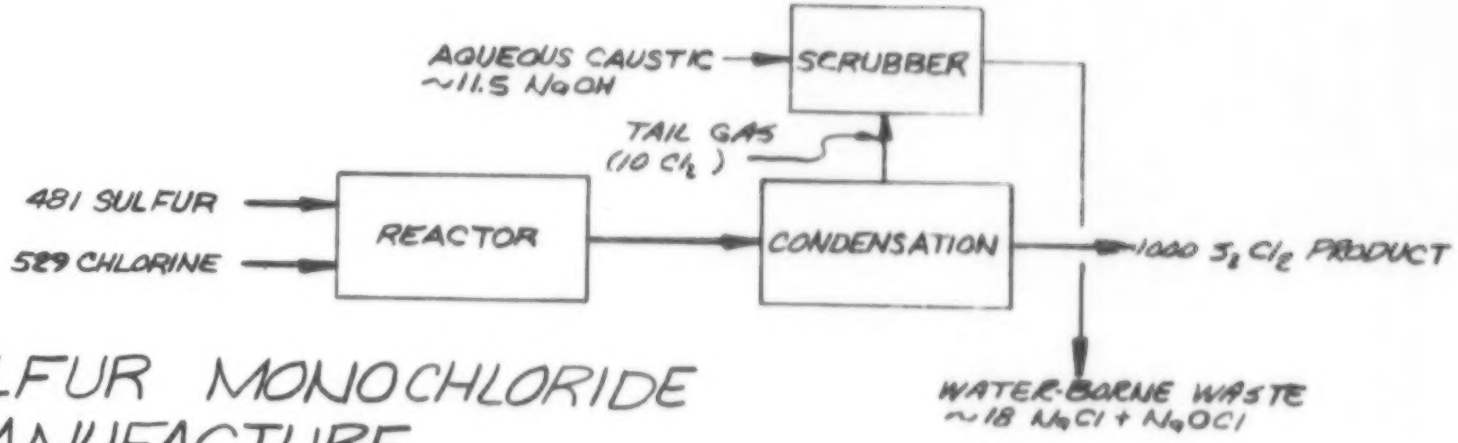
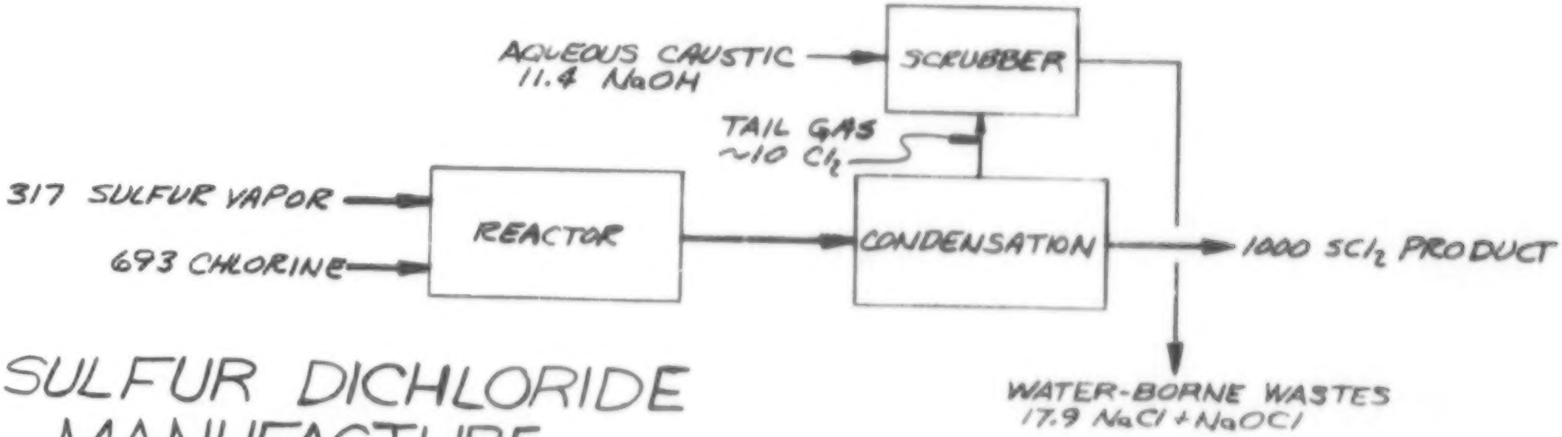


FIGURE 5-121
SULFUR DIOXIDE MANUFACTURE



SULFUR MONOCHLORIDE MANUFACTURE



SULFUR DICHLORIDE MANUFACTURE

FIGURE 5-122

and the SO_2 co-product. The only potentially hazardous solid wastes produced are spent catalyst ($SbCl_3$) contaminated with products and reactants. This material requires considerable care in handling, but, as the production of thionyl chloride by this process is limited to one plant, the quantities involved are very small. The properties of $SbCl_3$ are discussed in Appendix A. In the second process, phosgene ($COCl_2$) and SO_2 are reacted in the gas phase over a charcoal activated carbon catalyst. The product, thionyl chloride, is then condensed from the gas phase, collected, and packaged. The only wastes are spent activated carbon contaminated with the gases and wastes from scrubbing the tail gases.

This latter is a water-borne waste, while the former is generated in very small amounts at only one site and is not judged to be present in hazardous amounts.

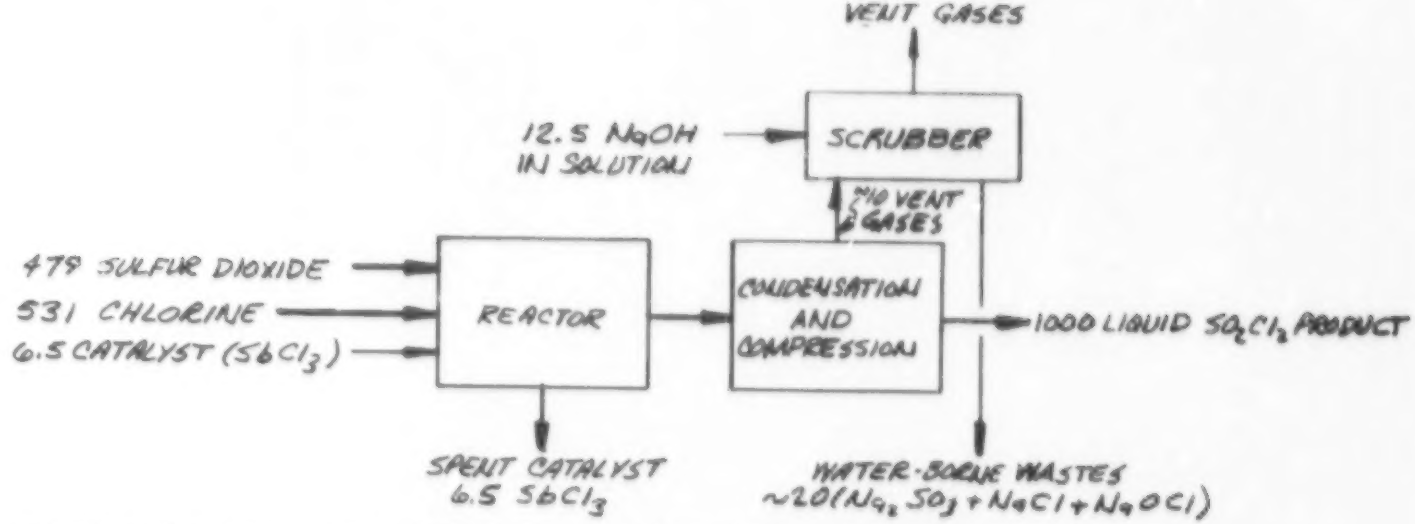
Sulfuryl Chloride (SO_2Cl_2)

Sulfuryl chloride (SO_2Cl_2) is produced by gas phase reaction of SO_2 with chlorine. The product is separated from the gas phase of condensation. The only wastes arise from tail gas scrubbing operations and from the catalysts used. None of these are judged to be hazardous. Flow diagrams for these sulfur compounds are given in Figure 5-123.

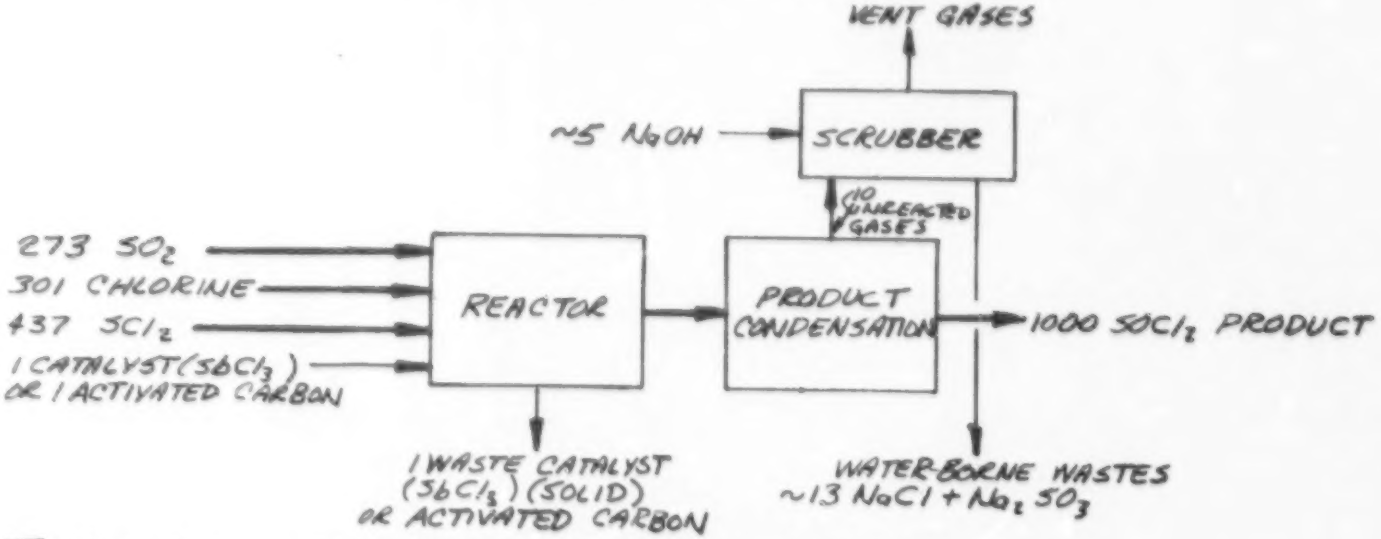
5.5.7.34 Thallium Compounds

These items are produced at only one facility in the U. S. using lead and zinc smelter flue dusts as a starting material. Specifically, the dusts are first dissolved in sulfuric acid and the lead and zinc values are collected and reused. The purified solutions are then electrolyzed to recover a cadmium-thallium alloy, from which the thallium is selectively leached. The leachate is then converted to thallic sulfate solutions, part of which is used to recover a solid salt product and the remainder being electrolyzed to recover the metal (a non-ferrous metallurgical process not in SIC 281).

The only heavy-metal-salt-containing wastes, which are not reprocessed internally, consist of the very dilute spent electrolysis solutions, a waste not attributable to SIC 281. These are generally given chemical treatment to remove the small amounts of heavy metal salts, and then landfilled. The heavy metals involved in this small waste are the oxides and hydroxides of such metals as cadmium and lead. Their properties are detailed in Appendix A.


VENT GASES
12.5 NaOH IN SOLUTION
SCRUBBER
~10 VENT GASES
479 SULFUR DIOXIDE
531 CHLORINE
6.5 CATALYST ($SbCl_3$)
REACTOR
CONDENSATION AND COMPRESSION
1000 LIQUID SO_2Cl_2 PRODUCT
SPENT CATALYST 6.5 $SbCl_3$
WATER-BORNE WASTES ~20(Na_2SO_3 + NaCl + NaOCl)

SULFURYL CHLORIDE MANUFACTURE


VENT GASES
~5 NaOH
SCRUBBER
10 UNREACTED GASES
273 SO_2
301 CHLORINE
437 SCl_2
1 CATALYST ($SbCl_3$) OR 1 ACTIVATED CARBON
REACTOR
PRODUCT CONDENSATION
1000 $SOCl_2$ PRODUCT
1 WASTE CATALYST ($SbCl_3$) (SOLID) OR ACTIVATED CARBON
WATER-BORNE WASTES ~13 NaCl + Na_2SO_3

THIONYL CHLORIDE MANUFACTURE

FIGURE 5-123

For the production of thallium compounds, other than the sulfate, the sulfate is first converted to the carbonate as shown in Figure 5-124 and the carbonate is then recovered and reacted with the appropriate mineral acid to generate the desired compound. There are no solid wastes generated by any of these processes. The total production of thallium compounds in the U. S. is less than eight tons per year.

5.5.7.35 Tin Compounds

As shown in Figure 5-125, stannous chloride is made by reaction of tin with hydrogen chloride followed by crystallization. No wastes are produced.

Stannic oxide is generated by either a dry or a wet process. The dry process involves calcination of the hydroxide as shown in Figure 5-126. All dusts are collected from vent gases via dry collection methods and returned to the process. The wet process (used by only one company which considers it proprietary) involves recovery of tin values from such waste materials as sodium stannate. This material is then converted to the dioxide. In this second process, all of the wastes are water-borne. The sludges from treatment of these wastes are sold for their tin content and the water-borne waste is discharged. Future plans for this process call for modification so as to use pure tin instead of scrap. This will eliminate the need for chemical pretreatments and, hence, the waste sludge. Thus there are no present or future hazardous wastes for land disposal.

5.5.7.36 Thiocyanates

Alkali metal thiocyanates are produced by reaction in solution of sulfur with the corresponding metal cyanides. All of the wastes generated are water-borne and treated by either biological or chemical means.

5.5.7.37 Zinc Compounds

As shown in Figure 5-127, zinc sulfate is made by reaction of zinc oxide with sulfuric acid. The zinc oxide is leached with sulfuric acid and filtered to remove insolubles. This solution is treated with zinc dust to precipitate metallic impurities, filtered, evaporated to dryness, and sold as the monohydrate. Some solid wastes are produced by product purification steps, but contacts with the industry have revealed that the wastes are always sold for their lead and cadmium values and are not discarded.

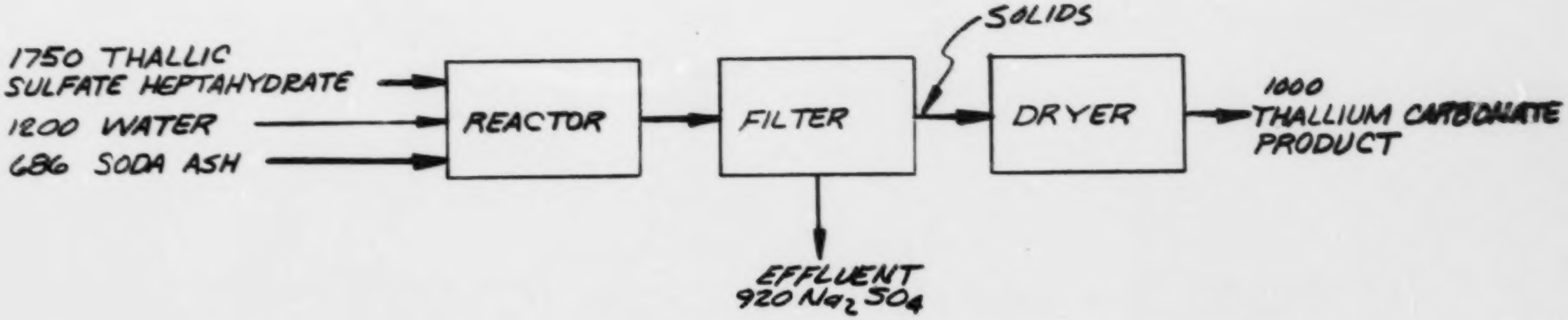


FIGURE 5-124
THALLIUM CARBONATE MANUFACTURE

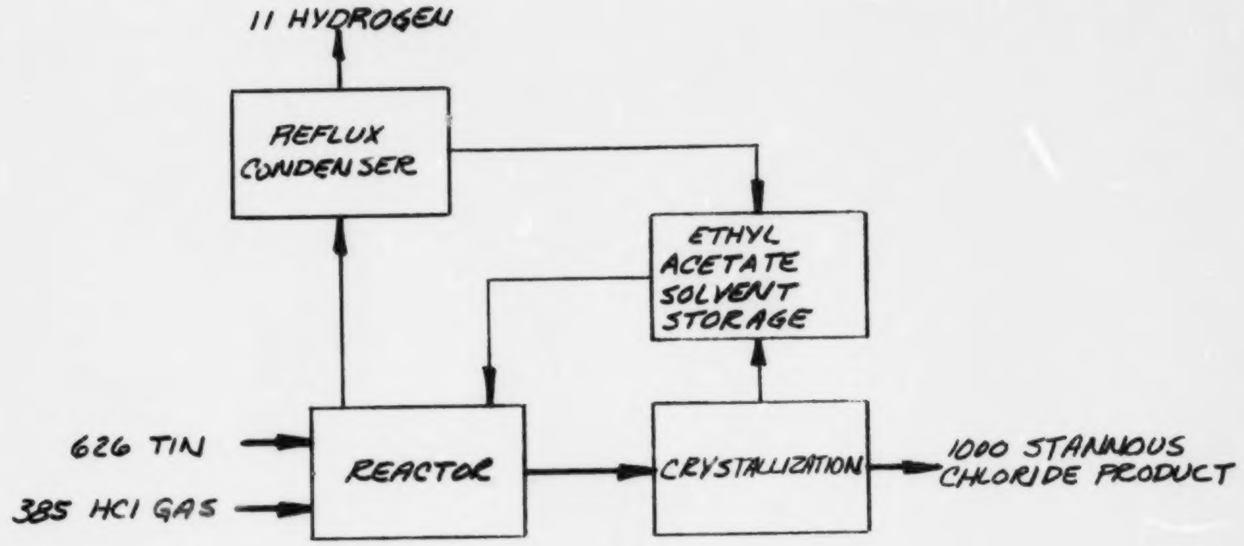


FIGURE 5-125
STANNOUS CHLORIDE MANUFACTURE

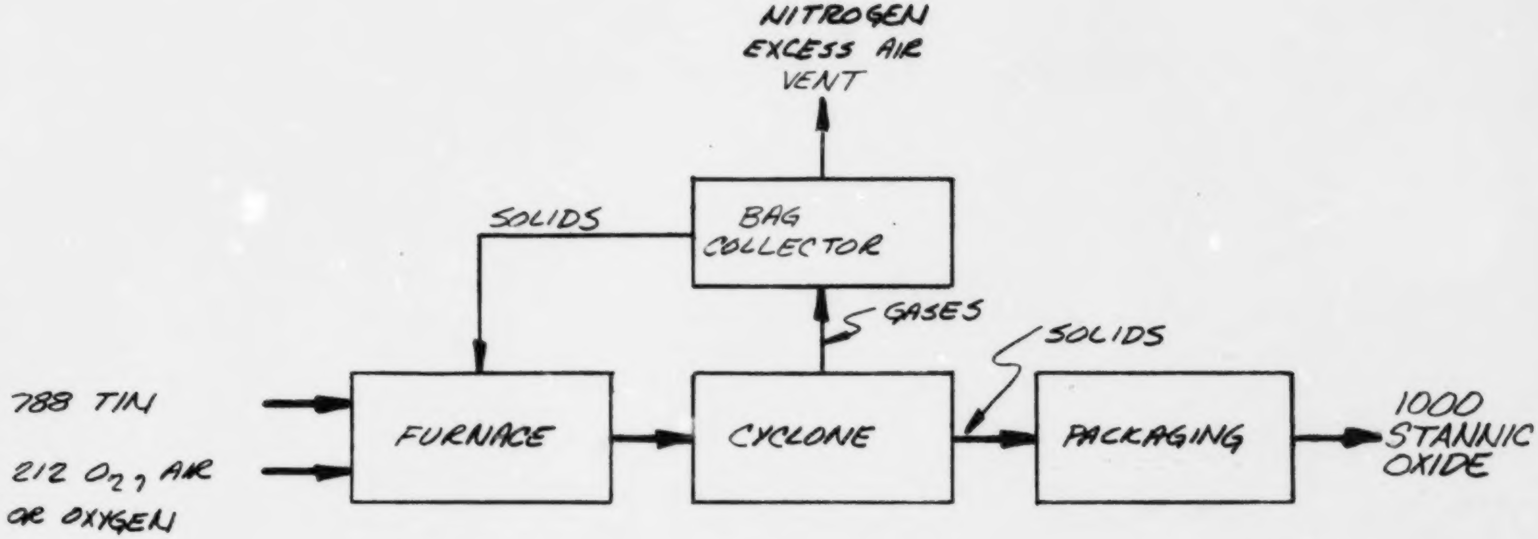


FIGURE 5-126
STANNIC OXIDE MANUFACTURE
DRY PROCESS

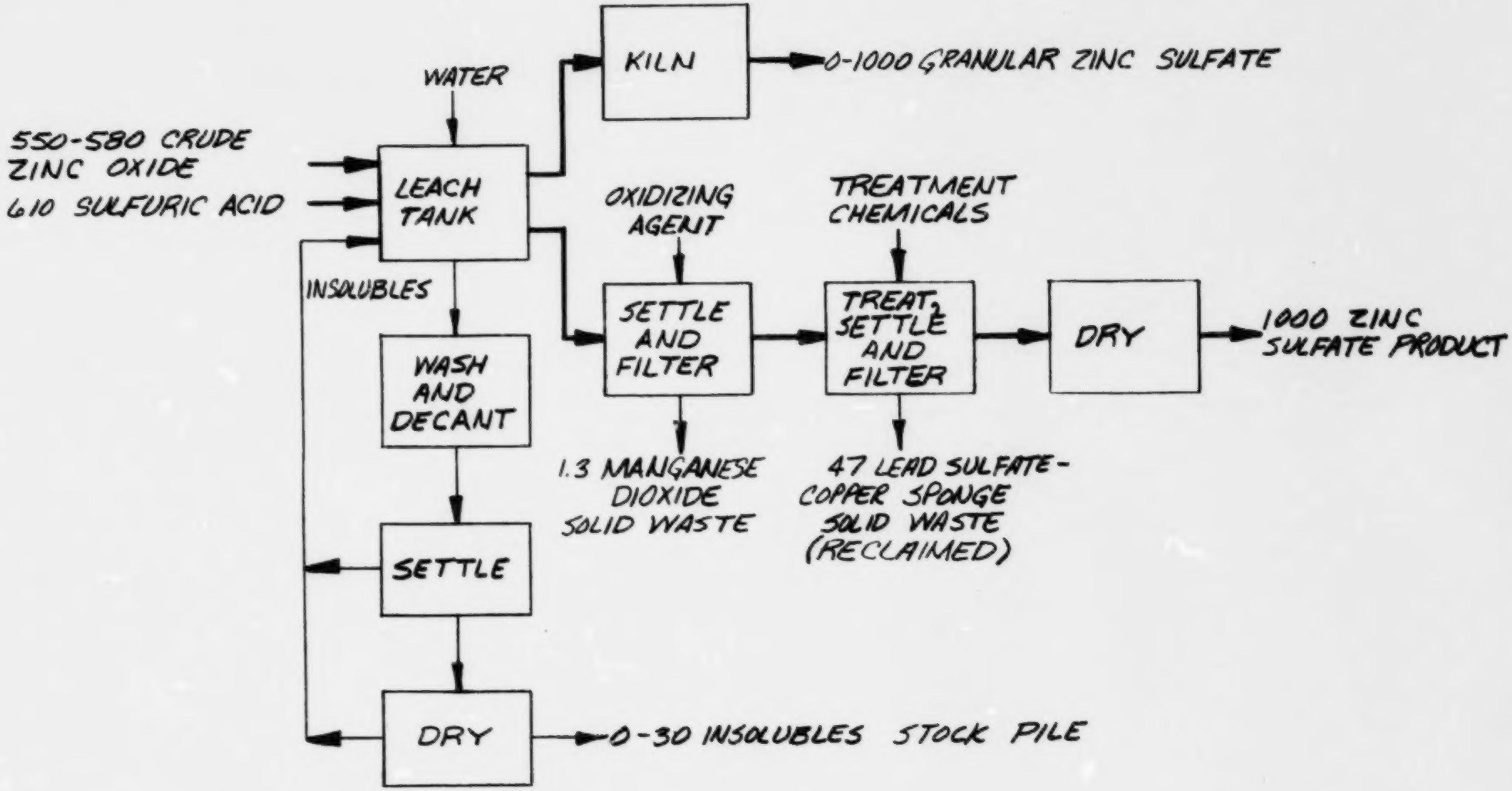


FIGURE 5-127

ZINC SULFATE MANUFACTURE

All other zinc salts are prepared by reaction of zinc oxide or zinc metal with the appropriate mineral acid. The only wastes are product purification solids which are generally reprocessed to reclaim lead and cadmium values. Figure 5-128 shows the typical manufacturing process for zinc chloride.

5.5.7.38 Aggregate of Hazardous Wastes From SIC 28199 Destined for Land Disposal

Of the large number of diverse inorganic chemical products in this industry subcategory, manufacture of the following products has been found to generate significant hazardous waste streams that are disposed of on land:

chromates

iron cyanide compounds

nickel sulfate

phosphorous

phosphorous pentasulfide

phosphorous trichloride

The aggregate hazardous waste streams to land disposal and the hazardous ingredients contents are given in Table 5-12 on a state-by-state, regional, and national basis. The iron cyanide hazardous waste is not given in Table 5-12 because it is a very small amount (1.5 kkg/yr) at one location (Washington state, electrolytic hydrogen peroxide manufacture).

5.5.7.39 Projection of Hazardous Wastes From SIC 28199 Destined for Land Disposal

In both chromates and nickel sulfate manufacture, the imposition of water regulations will bring more chromate-contaminated solid waste material to land disposal. This effect together with an estimated 4 percent per year growth in production through 1983 are the factors on which the waste projections in these segments were based.

The electrolytic process of manufacture of hydrogen peroxide will not expand in production volume in years to come since it is agreed by industry to be an outmoded technology. Although no plans have been divulged by industry to shut down the one remaining plant, we estimate that it will be on standby by 1977 and hence no hazardous iron cyanide wastes to land are projected from SIC 28199 for 1977 and 1983.

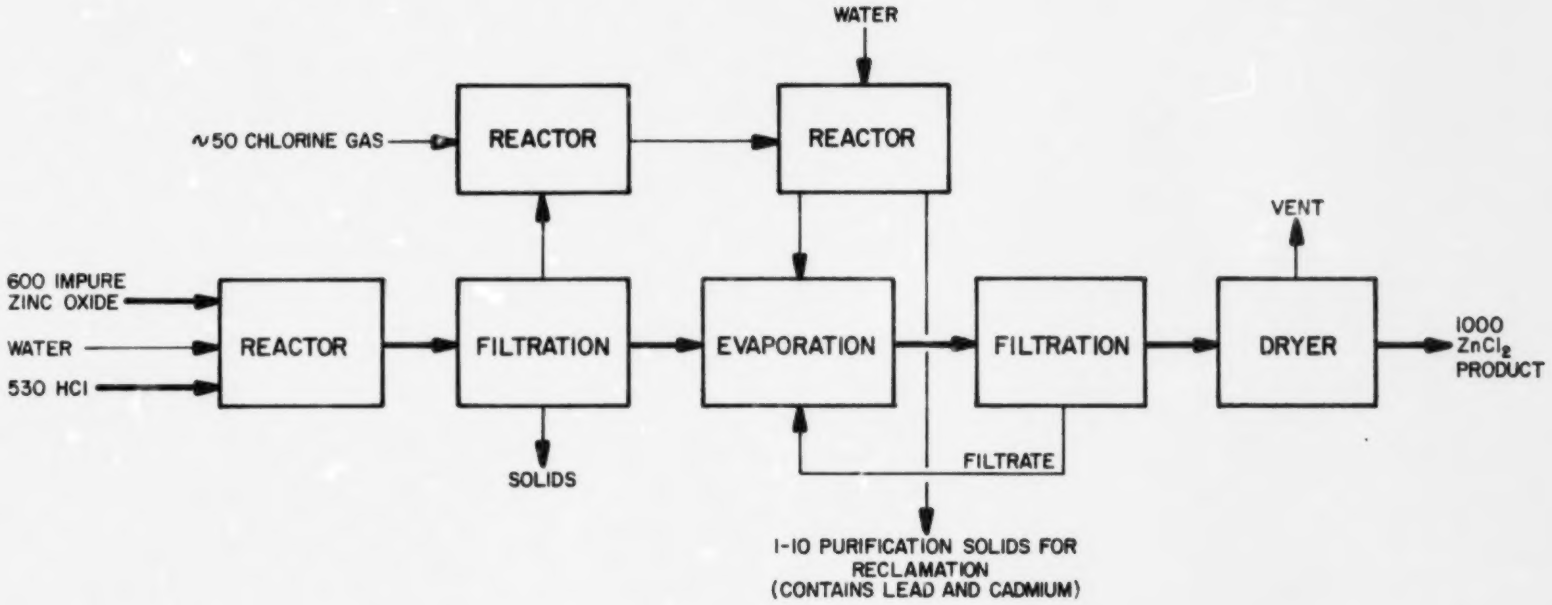


FIGURE 5-128
ZINC CHLORIDE MANUFACTURE

Table 5-12. Hazardous Wastes Currently Destined for Land Disposal From SIC 28199 Other Industrial Inorganic Chemicals, N.E.C., (metric tons per year, dry basis)

		Chromates		Nickel Sulfate		Phosphorus and Compounds				28199
		Total Hazardous Waste	Chromium Content	Total Hazardous Waste	Nickel Content	Total Hazardous Waste	Arsenic Content	Fluoride Content	Phosphorus Content	Total Hazardous Waste
IV	Alabama					12,600	0.4	1,100	340	12,600
X	Alaska									
IX	Arizona									
VI	Arkansas									
IX	California			0.1	0.02					0.1
VIII	Colorado									
I	Connecticut									
III	Delaware									
IV	Florida					13,000		1,100	350	13,000
IV	Georgia									
IX	Hawaii									
X	Idaho					81,000		6,900	2,200	81,000
V	Illinois					60	0.9		4.1	60
V	Indiana			2.0	0.4					2
VII	Iowa									
VII	Kansas									
IV	Kentucky									
VI	Louisiana									
I	Maine									
III	Maryland	64,000	0.14							64,000
I	Massachusetts									
V	Michigan									
V	Minnesota									
IV	Mississippi					13	0.1		1.0	13
VII	Missouri	2,000	0.003	0.1	0.02					2,000
VIII	Montana					14,200		1,200	380	14,200
VII	Nebraska									
IX	Nevada									
I	New Hampshire									
II	New Jersey	3,000	0.007	0.1	0.02	10	0.1		0.7	3,000
VI	New Mexico									
II	New York			0.1	0.02	30	0.5		2.1	30
IV	North Carolina	48,000	0.1							48,000
VIII	North Dakota									
V	Ohio			2.0	0.4					2
VI	Oklahoma									
X	Oregon									
III	Pennsylvania					15	0.3		1.0	15
I	Rhode Island									
IV	South Carolina					1	0.2			1
VIII	South Dakota									
IV	Tennessee					73,000	0.1	6,200	2,000	73,000
VI	Texas	40,000	0.09	0.1	0.02					40,000
VIII	Utah			0.3	0.06					0.3
I	Vermont									
III	Virginia									
X	Washington									
III	West Virginia					2	0.4			2
V	Wisconsin									
VIII	Wyoming									
TOTAL		160,000	0.34	5.6	0.9	190,000	3	16,500	5,300	350,000
Region I										
	II	3,000	0.007	0.2	0.04	40	0.6		2.8	3,000
	III	64,000	0.14			17	0.7		1.0	64,000
	IV	48,000	0.1			99,000	0.8	8,400	2,700	150,000
	V			4.0	0.8	60	0.9		4.1	64
	VI	40,000	0.09	0.1	0.02					40,000
	VII	2,000	0.003	0.1	0.02					2,000
	VIII			0.3	0.06	14,200		1,200	380	14,000
	IX			0.1	0.02					0.1
	X					81,000		6,900	2,200	81,000

Phosphorus and the two phosphorus chemicals, phosphorus pentasulfide and phosphorus trichloride, were projected on the basis of a 3.5 percent growth in production through 1983. Air and water regulations will not add to amounts of land-destined hazardous wastes from phosphorus pentasulfide and trichloride manufacture.

In phosphorus manufacture, a relatively small amount of solids will be added to the land-destined hazardous wastes by the effects of regulations.

The aggregate projections to 1977 are given in Table 5-13 and to 1983 in Table 5-14. The trend in hazardous wastes to land disposal in SIC 28199 can be summarized in terms of metric tons per year (short tons per year) as follows:

Period	Current	1977	1983
Dry basis	350,000 (390,000)	390,000 (430,000)	440,000 (490,000)
Moisture included	700,000 (770,000)	800,000 (880,000)	900,000 (990,000)

Table 5-13. Hazardous Wastes Expected to Be Destined for Land Disposal in 1977 From SIC 28199 Other Industrial Inorganic Chemicals, N.E.C. (metric tons per year, dry basis)

		Chromates		Nickel Sulfate		Phosphorus and Compounds				28199
		Total Hazardous Waste	Chromium Content	Total Hazardous Waste	Nickel Content	Total Hazardous Waste	Arsenic Content	Fluoride Content	Phosphorus Content	Total Hazardous Wastes
IV	Alabama					14,000		1,200	370	14,000
X	Alaska									
IX	Arizona									
VI	Arkansas									
IX	California			0.1	0.02					0.1
VIII	Colorado									
I	Connecticut									
III	Delaware									
IV	Florida					15,000		1,200	390	15,000
IV	Georgia									
IX	Hawaii									
X	Idaho					90,000		7,700	2,200	90,000
V	Illinois					60	1.0		4.5	60
V	Indiana			2	0.4					2
VII	Iowa									
VII	Kansas									
IV	Kentucky									
VI	Louisiana									
I	Maine									
III	Maryland	72,000	0.15							72,000
I	Massachusetts									
V	Michigan									
V	Minnesota									
IV	Mississippi					14	0.2		1.1	14
VII	Missouri	2,000	0.004	0.1	0.02					2,000
VIII	Montana					16,000		1,300	380	16,000
VII	Nebraska									
IX	Nevada									
I	New Hampshire									
II	New Jersey	3,000	0.008	0.1	0.02	16	0.1		0.8	3,000
VI	New Mexico									
II	New York			0.1	0.02	30	0.5		2.3	30
IV	North Carolina	54,000	0.11							54,000
VIII	North Dakota									
V	Ohio			2	0.4					2
VI	Oklahoma									
X	Oregon									
III	Pennsylvania					15	0.4		1.1	15
I	Rhode Island									
IV	South Carolina					1	0.2			1
VIII	South Dakota									
IV	Tennessee					81,000	0.2	6,800	2,000	81,000
VI	Texas	45,000	0.1	0.1	0.02					45,000
VIII	Utah			0.3	0.06					0.3
I	Vermont									
III	Virginia									
X	Washington									
III	West Virginia					2	0.4			2
V	Wisconsin									
VIII	Wyoming									
TOTAL		180,000	0.4	6	0.9	220,000	3.0	18,000	5,300	390,000
Region I										
II		3,000	0.008	0.2	0.04	46	0.6		3.1	3,000
III		72,000	0.15			17	0.8		1.1	72,000
IV		54,000	0.11			110,000	0.6	9,200	2,800	160,000
V				4.0	0.8	60	1.0		4.5	64
VI		45,000	0.1	0.1	0.02					45,000
VII		2,000	0.004	0.1	0.02					2,000
VIII				0.3	0.06	16,000		1,300	380	16,000
IX				0.1	0.02					0.1
X						90,000		7,700	2,200	90,000

Table 5-14. Hazardous Wastes Expected to be Destined for Land Disposal in 1983 From SIC 28199 Other Industrial Inorganic Chemicals, N.E.C., (metric tons per year, dry basis)

	Chromates		Nickel Sulfate		Phosphorus and Compounds				28199
	Total Hazardous Waste	Chromium Content	Total Hazardous Waste	Nickel Content	Total Hazardous Waste	Arsenic Content	Fluoride Content	Phosphorus Content	Total Hazardous Waste
IV Alabama					16,000		1,300	420	16,000
X Alaska									
IX Arizona									
VI Arkansas									
IX California			0.1	0.03					0.1
VIII Colorado									
I Connecticut									
III Delaware									
IV Florida					16,000		1,400	440	16,000
IV Georgia									
IX Hawaii									
X Idaho					100,000		8,500	2,700	100,000
V Illinois					80	1.2		5	80
V Indiana			3	0.4					3
VII Iowa									
VII Kansas									
IV Kentucky									
VI Louisiana									
I Maine									
III Maryland	80,000	0.2							80,000
I Massachusetts									
V Michigan									
V Minnesota									
IV Mississippi					20	0.2		1.4	20
VII Missouri	3,000	0.004	0.1	0.03					3,000
VIII Montana					18,000		1,500	470	18,000
VII Nebraska									
IX Nevada									
I New Hampshire									
II New Jersey	4,000	0.009	0.1	0.03	20	0.1		0.9	4,000
VI New Mexico									
II New York			0.1	0.03	40	0.6		2.6	40
IV North Carolina	60,000	0.13							60,000
VIII North Dakota									
V Ohio			3	0.4					3
VI Oklahoma									
X Oregon									
III Pennsylvania					20	0.4		1.4	20
I Rhode Island									
IV South Carolina					1	0.3			1
VIII South Dakota									
IV Tennessee					90,000	0.2	7,600	2,400	90,000
VI Texas	50,000	0.1	0.1	0.03					50,000
VIII Utah			0.4	0.06					0.4
I Vermont									
III Virginia									
X Washington									
III West Virginia					3	0.6			3
V Wisconsin									
VIII Wyoming									
TOTAL	200,000	0.4	6	1.1	240,000	3.6	20,000	6,400	440,000
Region I									
II	4,000	0.009	0.2	0.06	60	0.7		3.5	4,000
III	80,000	0.2			23	1.0		1.4	80,000
IV	60,000	0.13			120,000	0.7	10,000	3,300	180,000
V			6.0	0.8	80	1.2		5	86
VI	50,000	0.1	0.1	0.03					50,000
VII	3,000	0.004	0.1	0.03					3,000
VIII			0.4	0.06	18,000		1,500	470	18,000
IX			0.1	0.03					0.1
X					100,000		8,500	2,700	100,000

6.0 TREATMENT AND DISPOSAL TECHNOLOGY

Land-destined hazardous wastes from the inorganic chemicals industry, varying from high to low water content, originate either directly from the manufacturing processes or from air or water pollution control systems, and are usually in the form of slurries or wet solids. The technology used in their treatment and disposal depends for the most part on:

(1) The *volume* of hazardous waste involved. Small volume wastes can be treated and disposed of by almost any available technology without major economic impact. Large volume wastes often are not hazardous, but those that are can be significant economic impacts upon treatment and disposal.

(2) The *chemical composition* of the waste. Both the hazardous chemicals involved and the concentrations in which they are found determine the treatment and disposal technology required.

(3) *Geographical location*. Both the technology and the costs for land disposal are more favorable in the dry portions of western U.S. than in eastern U.S. Where rainfall is slight, both liquid and solid hazardous wastes can be disposed of with less danger of environmental contamination. The numerous isolated, thinly populated western areas available for hazardous waste disposal also minimize the effect on the population. Therefore, treatment and disposal options must be considered in light of the ambient climate, geology and population pattern.

(4) *Availability of land*. Some plants have little or no on-site disposal space available. This factor influences both location and methods of treatment and disposal.

Table 6.0 summarizes the estimates of present distribution of hazardous wastes currently disposed of on land by the various segments of the industrial inorganic chemicals industry. Very small quantities of hazardous materials originating from atypical plants, (e.g., small volume of several pounds per year hazardous wastes, residues containing minuscule heavy metals concentration) are not included in this table. By their small volume and/or low potential hazardousness they can usually be disposed of readily and with small economic impact. These minor hazardous waste streams are discussed in Section 5.

In the following sections are given brief discussions of the current treatment and disposal practices in those segments of the industrial inorganic chemicals industry having significant hazardous wastes destined for land disposal.

Table 6-0. Summary of Current Land Disposal Of Hazardous Wastes

	Industry Subcategory	Total Amount, Dry Basis (metric tons per year)	Number and Type of Plants Land-Disposing
SIC 28121	Chlorine	57,000	38 Diaphragm Cell 28 Mercury Cell 5 Down's Cell
SIC 28161	Titanium Dioxide Pigment	150,000	8 Chloride Process
SIC 28162	White Pigments	240	1 Antimony Oxide
SIC 28163	Chrome Colors	8,000	8 Chrome Pigments or Chrome Pigments/Iron Blues Complexes
SIC 28194	Inorganic Acids	1,400,000	12 Hydrofluoric Acid
SIC 28196	Aluminum Compounds	32,000	6 Aluminum Fluoride
SIC 28197	K and Na Compounds	4,400	3 Sodium Silicofluoride
SIC 28199	Others NEC	350,000	3 Chromates 4 Nickel Sulfate 10 Phosphorus 7 Phosphorus Pentasulfide 5 Phosphorus Trichloride

6.1 Treatment and Disposal in Alkalies and Chlorine Manufacture (SIC 2812)

The only segments of this subcategory having significant land-destined hazardous wastes are the three major chlorine manufacturing processes, the Diaphragm Cell Process, the Mercury Cell Process and the Down's Cell Process.

6.1.1 Diaphragm Cell Process

Three types of hazardous wastes can be generated by this process that may go to land disposal: asbestos, lead-contaminated treatment sludges, and chlorinated hydrocarbons. The latter, when not incinerated or disposed of in adjacent organic chemicals manufacture, are generally landfilled in drums or sent to disposal contractors. The asbestos- and lead-contaminated solid wastes and sludges are generally sent to landfill or pond disposal on-site. The treatment generally consists of a greater or lesser amount of segregation and dewatering prior to disposal. Of the 38 plants using this process known to be land disposing hazardous wastes, 21 use on-site landfills, 11 use on-site pond storage, and 11 send wastes to contractors having general purpose landfills.

Five plants incinerate their chlorinated hydrocarbons and 3 plants sewer them. Twenty-five plants have either negligible chlorinated hydrocarbons or do not separate them from the products. In any event, the amounts of chlorinated hydrocarbons generated from these industries are small, and are the product of diaphragm cell circuits where treated graphite is used.

The lead-contaminated wastes are ponded on-site in 11 plants, land-filled on-site in 3 plants and off-site in 2 plants. An estimated 22 plants generate no lead-contaminated wastes for land disposal.

6.1.2 Mercury Cell Process

Mercury-contaminated wastes and chlorinated hydrocarbons are the hazardous wastes generated by this process. Of 28 plants having land-destined hazardous wastes from this process, one plant retorts all mercury-containing sludges, 8 others retort the mercury-rich wastes only, and 4 are storing the high mercury sludges in drums until decisions are made on final disposal. One plant disposes of all sludges in a brine well off-site, and one plant sends mercury-rich sludges to contractors for recovery. This latter disposal is used by others occasionally.

Nine plants are now using on-site pond storage of sludges and 7 use on-site landfill. Four plants send wastes to contractors for secured landfilling. Several plants employ combinations of these treatment/disposal technologies.

Chlorinated hydrocarbon wastes from these plants are either not separated from product streams, separated and used elsewhere, or drummed for land storage.

6.1.3 Down's Cell Process

The principal hazardous waste stream from this process that may go to land disposal is the metallic sludges of sodium and calcium from the filtration of sodium product. These materials pose a hazard due to violent reaction with moisture, producing a possibility of explosion. However at both plants having this waste to dispose of barging to sea is used instead of land disposal. The other hazardous waste stream that is present at all sodium plants is sodium-contaminated cell rubble.

It should be pointed out that once this waste material has been thoroughly reacted with moisture, it is no longer hazardous in that sense. After reaction with atmospheric moisture and dissipation of the reaction products, the rubble waste is no longer hazardous.

6.2 Treatment and Disposal in Inorganic Pigments Manufacture (SIC 2816)

Significant amounts of land-disposed hazardous wastes are generated by several segments of this industry subcategory.

6.2.1 Titanium Dioxide-Chloride Process

Chromium-containing wastes are generated by this process by solubilizing of ore impurities and subsequent treatments.

Of the nine plants now generating such wastes, one deep-wells, one disposes at sea by barging, two send the wastes to contractors for off-site disposal, and 4 dispose on land by on-site ponding. The remaining plant is now discharging these wastes. Prior treatment in some cases consists of neutralization.

6.2.2 Antimony Oxide Manufacture

This SIC 28162 process generates land-disposed hazardous wastes at only one site. These antimony-rich wastes are stockpiled on-site at present, waiting for a final use, presumably by recovery. At present they constitute a waste, although in the long run this may be partially or completely eliminated.

6.2.3 Chrome Colors Manufacture

The plants and plant complexes manufacturing chrome pigments, iron blues and cadmium colors generate land-disposed hazardous wastes containing lead, chromium, zinc, cyanide and cadmium hazardous constituents. Of the 8 plants land-disposing such wastes, one disposed on-site by ponding and one by landfill after treatment, which consists principally of neutralization and precipitation. Six other plants use off-site disposal, one to municipal landfill, four to secured private landfill, and one to a land dump.

Two remaining chrome pigments plants do not land dispose, one claiming to recover all wastes and the other discharging.

6.3 Treatment and Disposal in the Manufacture of Miscellaneous Inorganic Chemicals (SIC 2819)

Several segments of this industry subcategory generate hazardous waste streams that may be disposed of on land. These wastes are contaminated with one or more of the following hazardous constituents: arsenic, fluoride, nickel, and phosphorus (elemental).

6.3.1 Manufacture of Inorganic Acids (SIC 28194)

Hydrofluoric acid manufacture generates fluoride-containing hazardous waste streams that are land-disposed. The principal fluoride constituent is calcium fluoride, which results from waste treatment by lime neutralization. Of the 12 plants generating such wastes, 6 are known to use on-site ponding disposal, 2 to use contractor general purpose landfills and one to send to a contractor who uses it for roadfill. The remainder is unknown.

Boric acid manufacture in only one location uses a process that generates wastes that go to land disposal. This waste is arsenic sulfide from product purification and wastewater treatment by sulfide precipitation. The waste is sent to secured municipal landfill.

6.3.2 Aluminum Fluoride

This SIC 28196 product is manufactured by a process that generates fluoride wastes. Waste treatment by liming produces calcium fluoride-containing hazardous waste streams for land disposal. One plant uses a unique proprietary process that generates no wastes of this sort. Of the remainder, 4 plants use on-site disposal by ponding or dumping and one uses a general purpose municipal landfill.

6.3.3 Sodium Silicofluoride

The manufacture of this SIC 28197 product generates fluoride-containing land-destined wastes similar to the foregoing. Of the 3 plants generating such wastes, one is known to deep-well the fluoride waste and one uses on-site pond disposal. The other is unknown.

6.3.4 Chromates Manufacture

Chromate-contaminated land-destined hazardous wastes are generated by the manufacture of these SIC 28199 products in 3 locations. One plant disposes of the chrome ore gangue off-site to a contractor for land and road construction purposes. One uses on-site land dumping and another uses approved private landfill.

6.3.5 Nickel Sulfate

Nickel-containing hazardous wastes for land disposal in relatively small amounts are generated by the manufacture of this SIC 28199 product. They result from the treatment of wastewaters by raising the pH to precipitate metallic salts. Two plants in this segment directly sewer their wastes. One plant uses on-site landfill for the precipitates, and another uses contractor landfill (general purpose).

6.3.6 Phosphorus, Furnace Process

Ten plants manufacturing this SIC 28199 product produce fluoride- and phosphorus-containing hazardous waste streams. These are universally disposed of on-site. The wastes result from water treatment. The phosphorus-containing wastes are settled on the bottom of storage ponds. Most plants endeavor to recover as much of the phosphorus as possible, although significant amounts remain. The fluoride wastes from scrubber water treatment are also settled in ponds. The fluoride is principally in the form of calcium fluoride from reaction with lime.

6.3.7 Phosphorus Pentasulfide

Several plants making this SIC 28199 product report no land-destined wastes. Treatment and disposal for these wastes, which are arsenic sulfide, phosphorus and phosphorus compounds, are specific to each company and the disposal technology is in a state of flux. Four plants presently landfill these wastes on-site; the other plants are drum storing their wastes pending further developments.

6.3.8 Phosphorus Trichloride

The arsenic trichloride waste from the purification of this 28199 product is generated in relatively small amounts. One plant uses on-site drum storage and two use on-site land dumping. Several plants report no land-destined hazardous wastes. The treatment and disposal of these wastes are also in a state of flux, and these latter plants are drum storing their wastes pending further developments.

6.4 Treatment and Disposal Technology Levels as Applied To Hazardous Wastes Generated by the Manufacture of Specific Chemicals

The following Tables 6-1 through 6-13 provide information on three identified levels of technology and disposal of hazardous wastes from the inorganic chemicals industry. These levels are characterized as follows:

Level I - Technology currently employed by typical facilities; i.e., broad average present treatment and disposal practice.

Level II - Best technology currently employed. Identified technology at this level must represent the soundest process from an environmental and health standpoint, currently in use in at least one (1) location. Installations must be commercial scale; pilot and bench scale installations are not suitable.

Level III - Technology necessary to provide adequate health and environmental protection. Level III Technology may be more or less sophisticated or may be identical with Level I or II Technology. At this level, identified technology may include pilot or bench scale processes providing the exact stage of development is identified.

The treatment and disposal of hazardous wastes from industries such as chlor-alkali, sodium, chrome pigments, iron blue, nickel sulfate, zinc chloride, sodium sulfides, titanium dioxide, and phosphorus chlorides and sulfides are currently in a state of flux and will change in the near future.

The large volume land-destined wastes that are no particular hazard and are presently land dumped and landfilled on-site will probably will continue being disposed of in much the same fashion.

Table 6-1. Chlor-Alkali-Diaphragm Cell Process

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Solids - Lead hydroxide or sulfide Asbestos fibers as slurry Liquids - Chlorinated hydrocarbons, where separated	Same as Level I	Same as Level I
Amount of Residual Wastes (kg/kkg product)	Approx. 1	Approx. 0.1	Same as Level II
Factors Affecting Hazardousness	Solubility of lead compounds changes with pH. Burning of hydrocarbons can result in explosions and air pollution if not properly done.	Same as Level I	Same as Level I
Treatment/Disposal Technology	1. Pond storage of lead precipitates, asbestos; burning of hydrocarbons. 2. Landfill lead precipitates and asbestos hydrocarbons not separated from product.	1. For those with carbon anodes: landfilling 2. For those with coated metal anodes: lead waste eliminated by in-process change; landfilling of asbestos; burning or recovery of chlorinated hydrocarbons (if any).	Same as Level II, except use approved landfill for asbestos and secured landfill for lead wastes.
Estimate of Number and % of Plants Now Using Technology	Approx. 19 plants (50%)	Approx. 19 plants (50%)*	None
Adequacy of Technology	Not adequate for future	Not adequate	Not proven
Non-land Environmental Impact	Possible ground and surface water contamination from lead and asbestos	Same as Level I	None
Problems and Comments	Lead and asbestos wastes should be reduced as new process technology of coated metal anodes and plastic cell membranes advance.	Same as Level I	Same as Level I
Compatibility with Existing Facilities	No process changes envisioned	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	None practiced	Same as Level I	Surface and groundwater monitoring for landfilling leachate. Air pollution monitoring for burning chlorinated hydrocarbons.
Installation Time for New Facility	Installed	Installed	One year
Energy Requirements	Slight - trucks and bulldozers for landfill.	Same as Level I	Same as Level I

*No further breakdown available since plants are presently converting from carbon anodes to coated anodes.

Table 6-2. Chlor-Alkali-Mercury Cell Process

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Mercury-containing sludges from various brine and water treatment sources. May contain elemental soluble or insoluble sulfides.	Mercury-containing sludges plus dry solids of low residual mercury content (retorting)	Dry solids of low (approx. 1-5 ppm) residual mercury content
Amount of Residual Wastes (kg/kkg product)	40-200 (wet slurry basis)	Mercury-containing sludges, 40-200 (wet basis); dry solids 15-20	15-20
Factors Affecting Hazardousness	Containment plus isolation performance of ponds, drums, and landfills. Leaching and pH control are factors for ponds and landfills	Containment and isolation performance of secured landfill. Mercury content of retorted dry solids.	Mercury content of dry solids.
Treatment/Disposal Technology	On-site storage and/or disposal using ponds, drums, landfills	A. Secured landfill, or B. Chemical extraction and secured landfill, or C. Retorting sludges, landfill residues. D. Combinations of the above.	A. Monitored retorting of all mercury-containing sludges plus landfilling of residues B. Secured landfill
Estimate of Number and % of Plants Now Using Technology	20 plants (71%)	A & B - 4 plants (14%); C - 9 plants (32%) 8 retort high mercury sludge only.	A. At least one plant is currently approaching this level. B. Secured landfill - 4 plants (14%)
Adequacy of Technology	Inadequate - storage in ponds and drums will decrease as improved technologies are utilized.	Adequate	Adequate.
Non-land Environmental Impact	Possible ground and/or surface water contamination through leaks and leachates.	Retorting releases some mercury vapor and sulfur oxides to the air. Adequate condensation and gas scrubbing is needed.	Same as Level II
Problems and Comments	Industry is in flux concerning the most economical and reliable ultimate disposal method.	Both secured landfilling and retorting are relatively expensive operations.	Some producers may find it more economical to contract for their sludge disposal.
Compatibility with Existing Facilities	No process modifications required.	Varies; retorting is usually an add-on to the end of brine and water treatment processes.	Same as Level II only with improved monitoring and control of operations.
Monitoring and Surveillance Techniques	Visual inspection of stored drums. Monitoring of ponds and landfill with wells.	A and B use monitoring wells and ambient surface water analysis. C monitors mercury content in air and ash, SO_2 content in air.	A. Monitoring of mercury content in retort ash and SO_2 and mercury in the air B. Monitoring used to maintain low mercury content
Installation Time for New Facility	Installed	Extraction and secured landfills - 1 year; Retorting facilities for all sludges - 2 years.	Same as Level II
Energy Requirements	Small - mainly trucks, bulldozers, pumps, and filter operations.	A and B - small, trucks and bulldozers; C - considerable fuel required for furance.	Considerable for retorting. This is a furnace roasting operation.

Table 6-3. Chlor-Alkali-Down's Cell Process

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	(1) Sodium calcium alloy sludge - reacts strongly with water to form caustic (2) Sodium contaminated rubble - same reaction	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg product)	(1) 0-13 (2) 50-80	Same as Level I	Same as Level I
Factors Affecting Hazardousness	Exposure of material to water under uncontrolled conditions.	Same as Level I	Same as Level I
Treatment/Disposal Technology	Land dumping and spreading of residues (item 2), barging and disposal at sea of item (1), where they are present.	Same as Level I except some plants practice recovery of sodium, calcium wastes, an in-process change.	Off-site contract disposal with controlled neutralization
Estimate of Number and % of Plants now using Technology	Sea disposal 2 plants (40%), rest only have contaminated rubble.	Same as Level I	None
Adequacy of Technology	Environmental adequacy of sea disposal in drums is controversial.	Same as Level I	Not proven
Non-land Environmental Impact	Possible personnel hazard from land dumping of residues.	Same as comments for Level I	Transportation hazard to burial site.
Problems and Comments	Sunken drums interfere with use of sea bottom, as in fishing. Land dump disposal requires proper handling to avoid hazards, until reactive materials are dissipated. Sea burial requires special disposal procedures in accordance with Coast Guard regulations.	Any required conversions to in-process recovery from current ocean dumping will require technology development and installations. Temporary on-site drum storage may be necessary until technology development and installations are completed.	This option is conceptualized and no contractor presently offers this service. This option has not been demonstrated
Compatibility with Existing Facilities	Compatible	See above comments	Compatible
Monitoring and Surveillance Techniques	A. Land dump leachate and drainage must be pH monitored. B. Sea disposal - special Coast Guard observation required.	Same as Level I	Same as Level I
Installation Time for New Facility.	None	Conversion from ocean dumping to recovery 2-3 years, but this is not a treatment disposal option, it is an in-process change.	2-3 years, if contractors are willing.
Energy Requirements	Small	Same as Level I	Small

Table 6-4 Titanium Dioxide - Chloride Process

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	A. Ore gangues are inert solids (i.e., silica) B. Waste treatment solids are mixed heavy metal oxides (mostly Fe) C. In some cases heavy metal salt solutions	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg product)	(Varies widely with ore). Inerts (ore gangue, i.e., SiO_2 + coke 160 avg) TiO_2 18 - >0 Other metal salts 130-1100* (as oxide)	Same as Level I	Same as Level I
Factors Affecting Hazardousness	A. For deep well disposal, the geology of the area determines seepage hazards B. Solubility of heavy metal salts vary - pH dependent.	Same as Level I	Same as Level I
Treatment/Disposal Technology	A. Land storage of ore gangue waste plus land storage of oxide wastes from wastewater treatment. B. Contract disposal of heavy metal salt solutions plus oxides generated by their treatment (Probably finally by landfill). C. Deep well disposal of concentrated process wastewaters. D. Ocean disposal**	Landfilling of ore plus landfilling of oxides generated by wastewater treatment in approved landfill	Same as Level II
Estimate of Number and % of Plants Now Using Technology	A. On-site land storage - 4 plants (50%) B. Contract disposal - 1 plant (12%) C. Deep well - 1 plant (12%) D. Ocean disposal - 2 plants (25%)	1 plant (12%)	Same as Level II
Adequacy of Technology	A. Burial of inerts is adequate. B. Deep well disposal is limited to areas having proper geology. C. Land storage of oxides may lead to leachate problems.	Adequate	Same as Level II
Non-land Environmental Impact	Burial of oxides or deep well disposal serves to abate surface water pollution problems. Burial sites and well sites should be closely monitored to eliminate sub-surface problems.	Same as Level I for burial sites	Same as Level II
Problems and Comments	Landfill is reliable under conditions where leaching can be avoided. Deep welling is limited by geological considerations.	Same as Level I for landfilling	Same as Level II
Compatibility with Existing Facilities	Deep well disposal, where geologically acceptable is an add-on operation not requiring additional land. Burial of oxide wastes may require use of an out of the plant disposal site.	Same as Level I for burial	Same as Level II
Monitoring and Surveillance Techniques	A. Deep well are not monitored for seepage (analysis for heavy metals). B. Burial sites also require similar monitoring.	Monitoring wells around landfill	Same as Level II
Installation Time for New Facility	Installed	1-2 years	Same as Level II
Energy Requirements	Deep well disposal - minor, for pumping of liquids only. Landfilling - minor for water pumping, pond dredging, trucking and burial.	Minor	Same as Level II

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*Note: These numbers are based on amounts of heavy (i.e., Fe, V, etc.) oxides that would be generated by wastewater treatment. Plants having higher amounts of heavy metal salts, deep well disposed such solutions in lieu of neutralization and landfilling.

**Since ocean barging is not an on-land disposal method, it is not costed in Section 7.

Table 6-5. Chrome Pigments and Iron Blue Manufacture

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Sludges of chromates, lead, zinc, cyanides, iron, chromium and other hazardous materials depending on product mix.	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg product)	150-250 (dry basis)* includes filter aids and calcium sulfate and water treatment precipitates.	Recovery reduces wastes by approx. 25%	Recovery by several plants will reduce wastes by approximately 50%.
Factors Affecting Hazardousness	Treatment and containment efficiency, product mix, pH level	Depends only on containment efficiency of landfill area.	Efficiency and containment of landfilling and chemical fixation operations.
Treatment/Disposal Technology	Off-site landfill	A. Secured landfill off-site	Same as Level II; or chemical fixation and landfilling (not proven).
Estimate of Number and % of Plants Now Using Technology	6 plants (60%)	4 plants (40%)	A. Planning secured landfill - 2 plants. B. Chemical fixation pilot stage.
Adequacy of Technology	Major improvements needed.	Adequate	All can be adequate
Non-land Environmental Impact	Both surface and ground water may be compromised.	None, except from failure of landfill integrity and possible water contamination.	None, except from failure of landfill, recovery or chemical fixation process.
Problems and Comments	This is one of the major problem areas in inorganic chemicals hazardous wastes. Large amounts of money have been spent in the past few years. Primarily on water quality. More attention is still needed.	Distinct progress has been made within the past 2 years in upgrading technology utilities.	Chrome pigments and iron blue are highed-valued chemicals worthy of recovery. Chemical fixation not proven.
Compatability with Existing Facilities	These are existing facilities.	Off-site facilities for land disposal may be required due to geology of available land considerations.	When facilities are cramped or secured landfill areas not available, recovery and/or chemical fixation may be desirable alternatives.
Monitoring and Surbeillance Techniques	Sampling and monitoring of surface water and ground water around ponds and land disposals.	Monitoring wells used around landfill and leachate control.	Same as Level II
Installation Time for New Facility	Installed	Monitoring installation time - 1 year.	Chemical fixation and recovery will take 2-3 years to evaluate and install.
Energy Requirements	Small - mainly pumping and transporting	Small - mainly pumping, transporting and landfilling.	Small - chemical fixation is a chemical reaction process rather than thermal or electrical.

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*Depends on product mix produced.

Table 6-6. Hydrofluoric Acid

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Solids formed from waste treatment are a mixture of silica, CaF_2, and gypsum.	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg of product)	2700-4325 $CaSO_4$ (3700 avg) 45-100 CaF_2 (75 avg) 1-27 silica (13 avg)	Same as Level I	Same as Level I
Factors Affecting Hazardousness	Solubility of CaF_2 limits degree to which fluoride can be reduced in waters, possibility of leachate problems.	Same as Level I	Same as Level I
Treatment/Disposal Technology	Lime treatment; pond storage or on-site landfill.	Pond storage (water treatment needs) and/or contract disposal (general).	Secured on-site landfill, leachate monitoring, rainwater diversion.
Estimate of Number and % of Plants Now Using Technology	9 plants (75%)	2 plant (22%)	None
Adequacy of Technology	Inadequate without pH and leachate control	Adequate if approved land site	Not proven
Non-land Environmental Impact	Leaching and runoff problems due to either runoff or improper pond pH control are possible, leading to water problems with dissolved fluorides.	Negligible with runoff collection and treatment and good pond pH control.	Same as Level II
Problems and Comments	Wastes are a mixture of co-product gypsum ($CaSO_4$) and CaF_2 along with minor amounts of silica. Plants producing HF frequently also produce sulfuric acid on-site and may also manufacture other fluorides.	Same as Level I	Same as Level I
Compatibility with Existing Facilities	Ponds and land available for disposal are present in all HF plants.	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	None	None	Need to monitor runoff waters for fluoride and pH
Installation Time for New Facility	Installed	Installed	On-site facilities for approved land storage - 1 year.
Energy Requirements	Small - for slurry pumping, dredging and piling of wastes.	Same as Level I	Same as Level I

Table 6-7. Boric Acid

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Sludge containing As_2S_3	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg of product)	Approximately 6	Same as Level I	Same as Level I
Factors Affecting Hazardousness	pH of ground water affects solubility of arsenic salt. Prepared secured landfills must be used.	Same as Level I	Same as Level I
Treatment/Disposal Technology	Burial off-site in secured landfills.	Same as Level I	Same as Level I
Estimate of Number and % of Plants Now Using Technology	1 plant (100%)	Same as Level I	Same as Level I
Adequacy of Technology	Satisfactory	Same as Level I	Same as Level I
Non-land Environmental Impact	None	Same as Level I	Same as Level I
Problems and Comments	None	Same as Level I	Same as Level I
Compatability with Existing Facilities	No problems.	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	Monitoring wells.	Same as Level I	Same as Level I
Installation Time for New Facility	None	Same as Level I	Same as Level I
Energy Requirements	Minimal - trucking and burial costs only	Same as Level I	Same as Level I

Table 6-8. Aluminum Fluoride

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Mixture of alumina, gypsum, CaF_2, other inerts (silica, etc.) recovered from wastewater treatment	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg product)	Alumina 12-24*; gypsum 63-126; CaF_2 30-42; other inerts 4-6	Same as Level I	Same as Level I
Factors Affecting Hazardousness	A. pH of pond water B. Presence of other materials in waste piles which may form soluble fluorides C. Leachate problems	Same as Level I	Same as Level I
Treatment/Disposal Technology	A. Precipitation of fluorides, storage or on-site landfill B. Municipal landfill	Same as Level I (A)	A. Level I plus leachate monitoring and rain water diversion. B. Recycle and reuse of waterborne wastes (limited to certain types of complexes).
Estimate of Number and % of Plants Now Using Technology	A. 4 plants (67%) B. 1 plant (15%)	Same as Level I (A)	A. None B. 1 plant (15%)
Adequacy of Technology	Land storage alone is at best a temporary disposal method.	Same as Level I	Adequate
Non-land Environmental Impact	Storage of fluoride containing wastes, if not done properly can lead to leachate problems.	Same as Level I	Same as Level I
Problems and Comments	Ability to avoid leachate problems is limited by the solubility of CaF_2	Same as Level I	Same as Level I
Compatibility with Existing Facilities	Ponding and land storage facilities are already in existence at the plants.	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	None	Same as Level I	Runoff needs monitoring for fluoride
Installation Time for New Facility	Installed	Same as Level I	Monitoring and leachate control, 1-2 years.
Energy Requirements	Minimal water pumping, dredging solids from pond and piling.	Same as Level I	Same as Level I, for recycling, only minor pumping requirements.

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*These numbers are based on amounts of final products after wastewater treatment.

Table 6-9. Sodium Silicofluoride

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Fluorides (CaF_2 recovered with wastewater along with such larger amounts of gypsum)	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg product)	30-61 (as F^-)	Same as Level I	Same as Level I
Factors Affecting Hazardousness	pH of pond water (higher pH increases CaF_2 solubility)	Same as Level I	Same as Level I
Treatment/Disposal Technology	A. Common treatment of process wastewaters with those from adjacent H_3PO_4 production facilities; landfill B. Deep well disposal of all wastes	Same as Level I (A)	A. Land storage of solids generated by wastewater treatment with collection and treatment of runoff from storage piles. B. Deep welling in proper geology determined by cognizant authorities to be environmentally adequate.
Estimate of Number and % of Plants Now Using Technology	A. 1 plant (33%) B. 1 plant (33%)	Same as Level I (A)	Not Known
Adequacy of Technology	Land and/or pond storage of fluorides without correction of possible leachate problems can lead to fluoride waterborne discharges.	Same as Level I	Not proven
Non-land Environmental Impact	Possible leachate problems (fluorides)	Same as Level I	None
Problems and Comments	Wastewater treatment is limited by solubility of CaF_2. Land storage effectiveness also limited by rain runoff problems.	Same as Level I	Limited only by wastewater treatment effectiveness which reduces fluoride to solubility limits of CaF_2.
Compatability with Existing Facilities	All silicofluoride plants are attached to wet process H_3PO_4 facilities which have needed areas for large amounts of gypsum solid wastes.	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	None	Same as Level I	Monitoring required for both wastewater effluent and leachates (fluoride).
Installation Time for New Facility	Installed	Same as Level I	Deep welling 2-3 years
Energy Requirements	Minimal, only for pumping of aqueous wastes, dredging and piling of solid wastes.	Same as Level I	Same as Level I

Table 6-10. Chromates Manufacture - Ore Processing

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Slurry of ore residues. Calcium carbonate, chromates, various inorganic salts and iron and chromium oxides.	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg of product)	800-3500 (dry basis). Includes ore residues.	Same as Level I	Same as Level I
Factors Affecting Hazardousness	Effectiveness of chemical treatment to convert Cr^{+6} to Cr^{+3} and pH control affecting solubility of Cr^{+3}.	Same as Level I	Same as Level I
Treatment/Disposal Technology	On or off-site landfill	Chemical treatment plus filtration and approved off-site landfill.	Same as Level II with secure landfill
Estimate of Number and % of Plants Now Using Technology	1 plant on-site (33%) 1 plant off-site (33%)	1 plant (33%)	None
Adequacy of Technology	Not adequate. Landfill leaching possible.	Same as Level I	Not proven
Non-land Environmental Impact	Leaching into ground or surface water can occur.	Same as Level I	None
Problems and Comments	Massive quantities of chromium-containing muds or sludges constitute potentially hazardous land-destined wastes.	Same as Level I	Good filtration techniques need to be developed
Compatibility with Existing Facilities	Plants need large approved landfill areas for waste disposal. Not all plants have these facilities or places to develop them nearby.	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	Surface water analysis and ground water monitoring by means of wells.	Same as Level I	Same as Level I
Installation Time for New Facility	Installed	Installed	Monitoring and treatment installation 1-year
Energy Requirements	Moderate. Due to the large quantities of wastes that have to be excavated and landfilled.	Same as Level I	Same as Level I

Table 6-11. Nickel Sulfate

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Sludges containing nickel oxides and sulfides	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg product)	0-250	Same as Level I	Same as Level I
Factors Affecting Hazardousness	pH of waters in contact with the solids (soluble at low pH)	Same as Level I	Same as Level I
Treatment/Disposal Technology	A. Land disposal B. Sewer disposal	Same as Level I (A)	A. Off-site secured landfill in lined drums B. Chemical fixation by contractor (not proven)
Estimate of Number and % of Plants Now Using Technology	A. 1 plant (25%) B. 2 plants (50%)	Same as Level I (A)	None
Adequacy of Technology	Pond and land storage is inadequate due to leachate problems	Same as Level I	Not proven
Non-land Environmental Impact	Leachate problems possible with land or pond storage	Same as Level I	None
Problems and Comments	Leachate problems	Same as Level I	Problems only as related to economic recovery of nickel values from impure sludges
Compatibility with Existing Facilities	No problems	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	None	Same as Level I	Need to monitor around secured landfill
Installation Time for New Facility	Installed	Same as Level I	No installation required
Energy Requirements	Small, only for trucking and pumping	Same as Level I	Trucking for landfilling, some energy requirements for reprocessing

Table 6-12. Phosphorus Manufacture

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Aqueous suspensions and slurries of colloidal phosphorus stable except in presence of air. Scrubber wastes are fluoride, lime, calcium sulfates and phosphates.	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg of product)	10-500 (scrubber wastes plus phosphorus)	Same as Level I	Same as Level I
Factors Affecting Hazardousness	Settling efficiency of ponds to control phosphorus in water effluent and access of air to settled material. Leaching of fluorides from ponds and landfill.	Same as Level I	Possible solubility of landfilled wastes.
Treatment/Disposal Technology	Phosphorus stored on-site in ponds or recovered; scrubber wastes landfilled; precipitator dusts landfilled or recycled.	Same as Level I	Same as Level II, except phosphorous recovered or destroyed rather than pond stored and scrubber wastes to approved landfill
Estimate of Number and % of Plants Now Using Technology	10 plants (100%)	Same as Level I	None
Adequacy of Technology	Adequate for storage; but may give problems. Will require eventual disposal or recovery of colloidal phosphorus.	Same as Level I	Not proven
Non-land Environmental Impact	Surface and ground water contamination can occur.	Same as Level I	Provisions need to be made to avoid air pollution.
Problems and Comments	Ponds particularly in wet climates, can overflow, have dike failures, and other problems.	Same as Level I	Ponds are low cost storage facilities and can be designed to last for many years. Recovery may not be economical.
Compatibility with Existing Facilities	Most plants already have settling ponds.	Same as Level I	Recovery facilities would be add-ons.
Monitoring and Surveillance Techniques	None	Same as Level I	Air quality monitoring needed for retorting operation and analysis of residue prior to landfilling. Monitoring wells are needed.
Installation Time for New Facility	Installed	Same as Level I	Recovery facilities either prior to ponds or retorting, 2-3 years.
Energy Requirements	Small, primarily water pumping.	Same as Level I	Depends on recovery used. Retorting is furnace operation requiring fuel.

Table 6-13. Phosphorus Trichloride and Phosphorus Pentasulfide

Factor	Level I, Prevalent Technology	Level II, Best Available Technology	Level III, Adequate Health and Environmental Protection
Physical and Chemical Properties of Residual Wastes	Phosphorus plus P_2S_5 (P_2S_5) Arsenic trichloride (PCl_3)	Same as Level I	Same as Level I
Amount of Residual Waste (kg/kkg of product)	1-2 (P_2S_5); 0.3 (PCl_5)	Same as Level I	Same as Level I
Factors Affecting Hazardousness	Phosphorus and P_2S_5 are both flammable, P_4 and $AsCl_3$ are toxic volatile material. For later use, there is high solubility. Treatment is required prior to disposal.	Same as Level I	Same as Level I
Treatment/Disposal Technology	A. PCl_3 - arsenic heavy wastes are collected, treated, drummed, and buried. P_2S_5 wastes (P_4 & P_4S_3) are typically drummed and buried.	Same as Level I	Same as Level II, except burial sites should be secured landfills
Estimate of Number and % of Plants Now Using Technology	PCl_3 - 5 plants (100%) P_2S_5 - 8 plants (100%)	Same as Level I	None
Adequacy of Technology	Inadequate	Same as Level I	Not proven
Non-land Environmental Impact	Problems will exist only if leaching occurs	Same as Level I	Same as Level I
Problems and Comments	There is no way to remove the toxicity from arsenic heavy materials. The best that can be achieved is to bury the material in such a manner that it cannot escape to the atmosphere. Reactive components need to be removed by treatment prior to burial.	Same as Level I	Same as Level I
Compatibility with Existing Facilities	Compatible	Same as Level I	Same as Level I
Monitoring and Surveillance Techniques	None	Same as Level I	Disposal site must be monitored for leachate (arsenic compounds). Leachates must be treated.
Installation Time for New Facility	Installed	Same as Level I	Burial facilities - 1 year
Energy Requirements	Minimal for packaging and burial only.	Same as Level I	Same as Level I

Although there are exceptions, most phosphorus, fluoride chemical, boron chemical and zinc oxide plants are located on large blocks of land in fairly isolated areas. For these general relatively large volumes of rather dilute hazardous wastes, increased monitoring, rainwater control and leachate control and treatment will be needed for many of the existing facilities, but except in exceptional cases, should not change the present on-site disposal pattern. There will also be increased utilization of present calcium sulfate and ore residue wastes for purposes of construction and raw material reclamation. The extent and timing for these developments can not be accurately forecast at this time.

Treatment and disposal of wastes may be expected to follow one or more of the following paths:

(1) More use of approved or secured landfill operations both on-site and by off-site contracting;
(2) Less dependence on ocean barging and deep well disposal;
(3) More recovery of valuable components such as mercury, chromates, nickel, zinc, sodium, chromium and vanadium;
(4) Conversion of present wastes to saleable products;
(5) More dependence on both on-site and off-site contractors who will assume total responsibility for hazardous waste treatment and disposal technology.

6.5 General Description of Present Treatment Technologies

The following describes existing treatment and disposal technology appropriate to the inorganic chemical industry:

6.5.1 Chemical Detoxification

Toxic or hazardous wastes are often treated chemically to reduce or destroy their hazardous nature. These treatments most often are included in water quality maintenance, but can be utilized for land-destined wastes as well, particularly by off-site contractors. The chemical reduction of hexavalent chromium wastes to trivalent is an example of chemical detoxification carried out in this industry category.

6.5.1.1 Neutralization

Acids and caustic wastes are reacted either with each other or with additional acid or caustic to form neutral salts. The resulting salts are usually less hazardous than either of the reactants. Also, the resultant salt may be insoluble and precipitate from the solution. Calcium salts derived from low cost limestone or lime are particular examples of limited solubility.

6.5.1.2 pH Control

The control of pH may be equivalent to neutralization if the control point is at or close to pH 7. Chemical addition to waste streams may be designed, however, to maintain a pH level on either the acidic or basic side for purposes of controlling desired reactions or solubility as shown by Figure 6-1 (12).

Examples of pH control being used for precipitating undesired pollutants are:

(1) $Cr^{+3} + 3OH^- = Cr(OH)_3$
(2) $Fe^{+3} + 3OH^- = Fe(OH)_3$
(3) $Mn^{+2} + 2OH^- = MnO_2 + 2H^+ + 4e^-$
(4) $Zn^{+2} + 2OH^- = Zn(OH)_2$
(5) $Ni^{+3} + 3OH^- = Ni(OH)_3$
(6) $Cu^{+2} + 2OH^- = Cu(OH)_2$

Reactions (1) and (2) are used for removal of chromium and iron contaminants involved with chromate reductions. Reaction (3) is used for removing manganese from permanganate and manganese sulfate water-borne wastes. Reactions (4), (5), and (6) are used on wastewater from nickel sulfate, copper salts and zinc salts of this study. It is estimated that approximately 1 percent of the 250,000 metric tons of concentrated hazardous wastes is treated in this manner.

6.5.1.3 Oxidation-Reduction Reactions

The modification or destruction of many hazardous wastes is accomplished by chemical oxidation or reduction reactions. Cyanides can be oxidized with chlorine or ozone to less hazardous cyanates or to final destruction to innocuous material. Hexavalent chromium is reduced to the less hazardous trivalent form with sulfur dioxide or bisulfites. Sulfites, with large COD values, can be oxidized with air to inert sulfates. These examples and many others are basic to the modification of inorganic chemicals water-borne wastes to make them less troublesome.

Cyanides

The two most common methods of treating cyanides are:
(1) single or two-stage alkaline chlorination and
(2) hypochlorite oxidation.

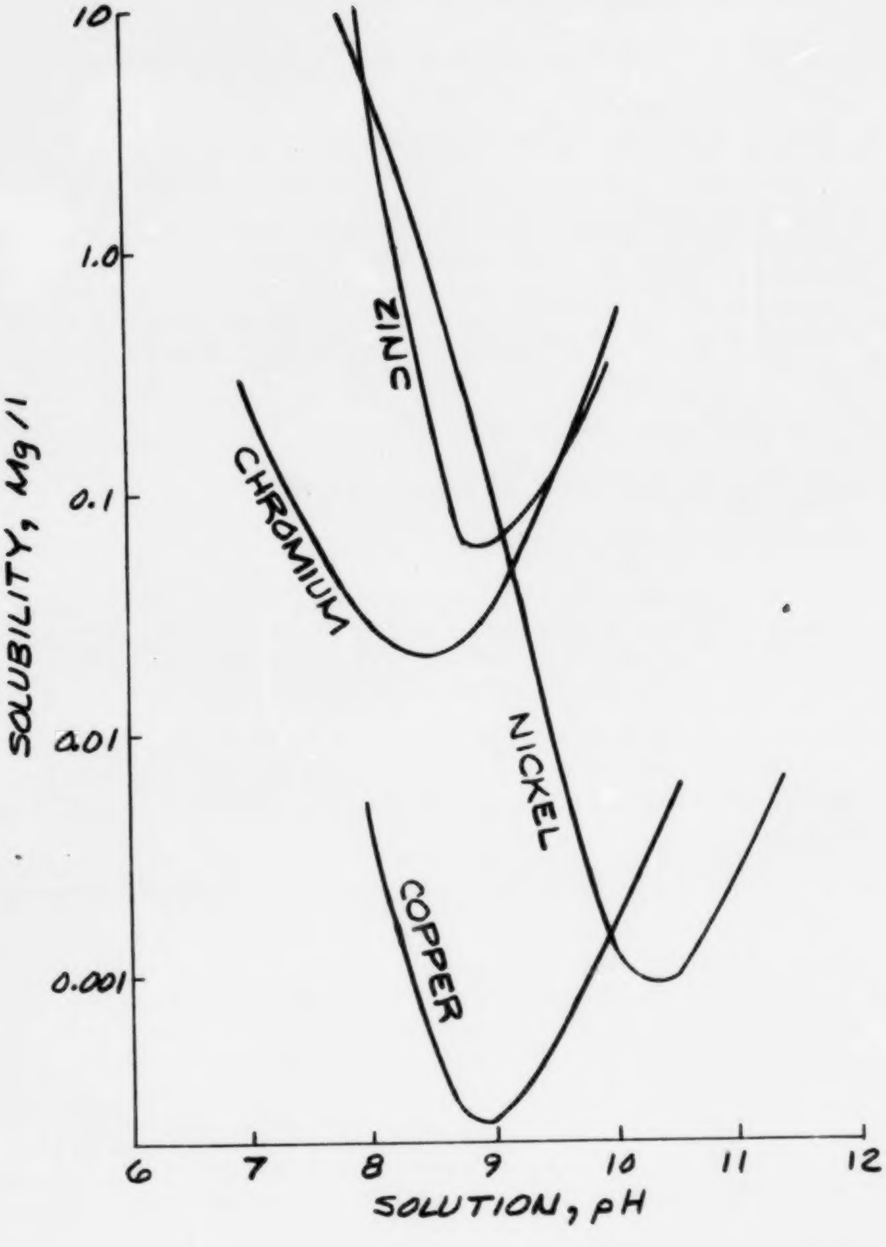

FIGURE 6-1
SOLUBILITY OF COPPER, NICKEL, CHROMIUM AND ZINC AS A FUNCTION OF SOLUTION pH

Alkaline Chlorination:

Stage 1 - 11.5 pH $NaCN + Cl_2 + 2NaOH = NaCNO + 2NaCl + H_2O$
(fast)

Stage 2 - 7.5 to 9.0 pH $2NaCNO + 3Cl_2 + 4NaOH =$
$N_2 + 2CO_2 + 6NaCl + 2H_2O$ (slow)

The stage 1 cyanates are stable and less toxic than cyanides (23). Stage 2 completes the destruction to nitrogen and carbon dioxide, but considerably more chlorine and caustic are required for the overall 2-stage process than for the single-stage oxidation to cyanate. The reaction is also slower.

Hypochlorite Oxidation

$2NaCN + Ca(OCl)_2 = 2NaCNO + CaCl_2$

$2NaCN + 2NaOCl = 2NaCNO + 2NaCl$

Either calcium or sodium hypochlorite can be used depending on economics and availability. For small plants or small cyanide wastewater loads, the recently developed electrical hypochlorite generators may be useful.

Both alkaline chlorination and hypochlorite treatments normally reduce oxidizable cyanide to essentially zero concentration. Complex cyanides are not usually affected.

Ozone has also been used for oxidation of cyanides (55). Other methods include boiling and peroxide decomposition (57).

Complex cyanides are much more resistant to oxidation or removal than simple cyanides. Soluble complex cyanides may often be removed by chemical precipitation with iron salts (such as ferrous sulfate) or other heavy metal ions (zinc or cadmium).

Ferro- and ferricyanides as well as other complex cyanides may be destroyed by either ozone or chlorine oxidation in acid solution. Ozone appears to be the best choice (15).

Complex cyanides are less toxic than oxidizable cyanides and are stable except to ultraviolet light (sunlight).

The proposed mechanism is:

$4Fe(CN)_6^{(-4)} + O_2 + 2H_2O = 4Fe(CN)_6(-3) + 4OH^-$

$4Fe(CN)_6^{(-3)} + 12H_2O = 4Fe(OH)_3 + 12HCN + 12CN^-$

Reported rate of oxidation of ferrocyanide in the presence of sunlight leaves about 25 percent of the original concentration in five days -- the ferrocyanide disappearing completely in 10-12 days.

Chromates

Chromates are reduced to less toxic Cr^{+3} compounds by such chemicals as sulfur dioxide (reaction 1), sodium metabisulfide (reaction 2), sodium bisulfite (reaction 3), sodium sulfite (reaction 4), ferrous sulfate (reaction 5), and ferrous chloride (pickle liquor) (reaction 6).

(1) $2H_2CrO_4 + 3SO_2 + 3H_2O = Cr_2(SO_4)_3 + 5H_2O$

(2) $4H_2CrO_4 + 3Na_2S_2O_5 + 3H_2SO_4 = 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 7H_2O$

(3) $4H_2CrO_4 + 6NaHSO_3 + 3H_2SO_4 = 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 10H_2O$

(4) $2H_2CrO_4 + 3Na_2SO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3Na_2SO_4 + 5H_2O$

(5) $2H_2CrO_4 + 6FeSO_4.7H_2O + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 50H_2O$

(6) $2H_2CrO_4 + 6FeCl_2 + 12HCl = CrCl_3 + 6FeCl_3 + 8H_2O$

These reactions go to virtual completion with limits of approximately 0.01 mg/liter residual chromate. Removal of the less toxic but still undesirable Cr^{+3} compounds is accomplished with pH control or precipitation on the basic side.

(7) $Cr^{+3} + 3OH^- = Cr(OH)_3$

Total chromium is a mixture of suspended $Cr(OH)_3$ plus residual dissolved chromate. Total chromium levels of 0.1 to 0.3 mg/liter can usually be attained since the suspended chromium hydroxide usually settles readily. Suspended chromium in the Cr^{+6} category may also be present from insolubles such as lead chromate or other chromates such as particulates of chrome pigments.

Inorganic Sulfur Compounds

Inorganic sulfur compounds range generally with degree of oxidation from the very harmful hydrogen sulfide to the relatively innocuous sulfate salts such as sodium sulfate. Intermediate oxidation steps include sulfides, thiosulfates, hydrosulfites, sulfites and finally sulfates.

Oxidation is accomplished with air, hydrogen peroxide, chlorine and other oxidizing agents.

(1) Sulfides (58)

Sulfides are readily oxidizable with air up to the thiosulfate level. Thiosulfates are less harmful than sulfides (of the order 1000 to 1) and approach the innocuousness of sulfates: $4S^- + 3O_2 = 2S_2O_3^{-2}$. Reaction level is 90-95 percent complete.

(2) Thiosulfates

Thiosulfates are difficult to oxidize further with air (54). They can, however, be oxidized to sulfates with powerful oxidizing agents such as chlorine and peroxides: $S_2O_3^{-2} + Cl_2 = 2SO_4^{-2}$; $S_2O_3^{-2} + H_2O_2 = 2SO_4^{-2}$. Reaction level should be 95-99 percent complete.

(3) Hydrosulfites

Hydrosulfites can also be oxidized by oxidizing agents such as Cl_2 and peroxide, and perhaps with catalyzed air oxidation: $S_2O_4^{-2} + Cl_2 = 2SO_4^{-2}$;$S_2O_4^{-2} + H_2O_2 = 2SO_4^{-2}$. Reaction level should be 90-99 percent complete.

(4) Sulfites

Sulfites are readily oxidized with air to sulfates at a 90-99 percent completion level. Chlorine and peroxides would be expected to perform similar oxidation: $2SO_3^{-2} + O_2 = 2SO_4^{-2}$.

6.5.1.4 Precipitations

This reaction of two soluble chemicals to produce insoluble or precipitated products is the basis for removing many undesired water-borne wastes. The use of this technique varies from lime treatments in order to precipitate sulfates, fluorides, hydroxides and carbonates to sodium or ferrous sulfide precipitations of copper, lead and other toxic heavy metals. Precipitation reactions are particularly responsible for heavy suspended solids loads. Removal of these suspended solids is accomplished by means of settling ponds, clarifiers and thickeners, filters, and centrifuges.

The following are examples of precipitation reactions used for waste-water treatment:

(1) $SO_4^{-2} + Ca(OH)_2 = CaSO_4 + 2OH^-$

(2) $2F^- + Ca(OH)_2 = CaF_2 + 2OH^-$
(3) $Na_2SiF_6 + 3Ca(OH)_2 = 3CaF_2 + SiO_2 + 2NaOH + 4H_2O$
(4) $BaS + FeSO_4 = BaSO_4 + FeS$
(5) $Zn^{+2} + Na_2CO_3 = ZnCO_3 + 2Na^+$
(6) $CrO_4^{-2} = + Pb^{+2} = PbCrO_4$
(7) $Cu^{+2} + Na_2S = CuS + 2Na^+$

6.5.2 Recovery and Reuse

Many toxic or hazardous inorganic chemicals wastes contain valuable materials. Whenever this is the case, recovery and reuse is one of the most desirable methods of hazardous waste avoidance. Silver, selenium, thallium, mercury, copper, lead, chromium, zinc and other heavy metals, once they are removed from water or air streams, are often recovered rather than land disposed. It is uneconomical to reclaim these metals only when they are very minor constituents of the waste or when the quality of the product is adversely affected as in chrome pigments manufacture. There are also private contractors that specialize in hazardous waste reclamation (1) (33) (36). In view of the fact that recovered and recycled materials are not land-destined, these do not appear in the earlier hazardous waste allocations in Section 5.0.

6.5.3 Disposal Ponds or Lagoons

Approximately ninety percent of the hazardous waste in the United States is in liquid or sludge form (47). It is likely that a similar percentage of close to ninety percent non-dry-solid hazardous waste exists for the inorganic chemicals industry as well.

Whenever feasible, pond or lagoon disposal of hazardous wastes is one of the simplest and most economical of approaches. It suffers from a number of restrictions, however:

(1) The pond needs to provide protection from both surface and groundwater contamination. With the exception of some pits in naturally impervious soil or in some very dry climates this means a lined pond. Liners include clay, plastic sheeting, asphalt, concrete, epoxy and other impervious materials, all of which are relatively expensive.
(2) Except for dry climates such as found in the western U.S., the ponds without discharge will eventually overflow from rainfall accumulation.
(3) Ponds are prone to be "flushed out" whenever massive rainfall and floods inundate the pond area. Here again,

it is difficult and expensive to provide flood protection, particularly in wet climates.

In view of these restrictions, disposal ponds and lagoons are usually feasible only in the western U.S. where evaporation disposal of a large volume per year of liquid waste is carried out. Ponds, in other regions,must be considered as storage ponds which will eventually need drainage cleaning or treatment and disposal action. Pond storage and disposal probably accounts for 20-30 percent of the total land-destined hazardous wastes. Pond storage of wastes occur, for example, in the manufacture of borax (SIC 2819), sodium silicofluoride (SIC 2819), dichromates (SIC 2819), boric acid (SIC 2819), and chlorine (SIC 2812).

6.5.4 Burning and Incineration

Since inorganic chemicals are generally non-combustible and their wastes are mainly found as sludges and liquids, burning or incineration is rarely used for treatment and disposal of inorganic hazardous wastes. A few small organic wastes are the exception. These account for less than 1 percent of the total wastes. An example from these industries is the incineration of chlorinated hydrocarbon wastes from the chlor-alkali industry (SIC 28121).

6.5.5 High Temperature Processing

Although not flammable, inorganic hazardous wastes in some cases can be decomposed, smelted, roasted, volatilized and/or distilled in fashion similar to recovery of metals from ores. Mercury can be driven from wastes by heating in furnaces and retorts, condensed in chilled heat exchangers and recovered. This is one of the more promising approaches to treatment of mercury sludges from the mercury cell chloralkali industry (23) (33). Smelting operations are also widely used for hazardous metallic wastes (35) (43). High temperature processing accounts for an estimated 1-2 percent of the total hazardous wastes.

6.5.6 Open Dumping

Open dumping of hazardous inorganic chemicals wastes into gravel pits, dumps and other uncontrolled disposal areas is still a disposal practice in a few isolated instances in these industires. Most of the companies producing inorganic chemicals contacted during both this study and previous water quality studies, however, have demonstrated increasing awareness and responsibility for treatment, control and disposal of hazardous wastes. According to information from both private contractors and interviewed inorganic chemicals

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producers, most chemical companies want no "surprises" from disposal and are checking closely on both their own and contract disposal sites and procedures.

Massive processing wastes such as ore residues and unsaleable by-products contribute a major portion (estimated 95 percent) of the potentially hazardous land-destined total waste volume for the inorganic chemicals industry. These large volume wastes, containing relatively small amounts of hazardous components, are currently land dumped or landfilled usually on-site. Examples of such wastes are ore and water treatment residues from the ore processing in chromates manufacture, calcium sulfate contaminated with calcium fluoride from the production of hydrogen fluoride, and ore residues fron the production of lead and zinc compounds. The large volume and the obviously high economic impact of more costly treatment and disposal technology make it necessary to consider each of these situations very carefully.

6.5.7 Municipal Sewers

Hazardous wastes from a number of inorganic chemicals manfacturers currently go into municipal sewer systems. These materials wind up in sewage sludge, some of which is destined for land disposal. Percentage of total volume of inorganic chemicals industry wastes being disposed of in this fashion is judged to be small (less than 1 percent).

6.5.8 Burial

Some quantities of inorganic chemicals industry hazardous wastes are disposed of by burial. These wastes include dry solids, sludges and liquids. Burial locations include specialized disposal sites such as abandoned mines, quarries, and government facilities, as well as public and private landfills.

Details are given later in Section 6.6.

6.5.9 Deep Well Injection

The deep well injection of hazardous inorganic chemicals includes acids, cyanides, heavy metal compounds, chromates and arsenates as well as a number of relatively innocuous inorganic salts.

Deep welling is a specialized form of land disposal of hazardous wastes. It is normally restricted to liquids only since suspended solids or sludges tend to clog the porous rock shale or sand structure into which the injection occurs.

Disposal of inorganic chemicals industry hazardous wastes by deep wells is done both on-site by the plants and off-site by contractors. Most of the contract disposal wells encountered were in southern locations such as Texas, Oklahoma, and Louisiana. Disposal wells are located in Florida and Tennessee and account for 14 percent of the total waste volume. Deep well injection of wastes is used, for example, at some plants manufacturing titanium dioxide pigment by the chloride process (SIC 28161).

6.5.10 Ocean Barging

Currently a number of hazardous wastes generated by the inorganic chemicals industry are disposed of by ocean barging. Some of these wastes will in the future be destined for land disposal. Sodium sludges, titanium dioxide wastes and small quantities of miscellaneous hazardous chemicals are among the materials currently involved.

Examples of current use of barging and disposal at sea in these industries occur in the manufacture of sodium (SIC 28121) and titanium dioxide pigment (SIC 28161).

6.6 On-site vs. Off-site Disposal

Of a total of 175 plant sites, an estimated 25 percent (35-45 plant sites) hire contractors for off-site disposal of at least a portion of their hazardous wastes. The remaining 75 percent treat and dispose of their own wastes. In general, contractors are used for small volume wastes, particularly in congested areas where treatment and disposal land is at a premium. Contractors account for 10-15 percent of the total volume disposed.

6.6.1 Specialized Disposal Sites

In the disposal of hazardous wastes, advantage is often taken of existing mines, quarries, abandoned government property and other facilities which have fortuitous geological and environmental isolation. For example, abandoned missile silos in Idaho are utilized by a private contractor for disposal of hazardous wastes (37). Clay pits in Ohio and California provide impervious liquid waste disposal sites (27).

In general, however, specialized disposal sites are not utilized to any significant degree by the inorganic chemicals industry (less than 0.2 percent).

6.6.2 Public and Private Landfills

Definitions of landfills that pertain to this means of disposal are:

General landfill: A site which is limited to disposal of inert solid wastes which should not pose a threat to water quality. The site may contain water (e.g., marshy areas, gravel pits, or periodically flooded areas) with no threat to water quality from the wastes.

Approved landfill: A site which is suitable for the disposal of inert solid wastes and decomposable organic materials. The site must provide separation of the wastes from underlying or adjacent usable water because of leachate possibilities.

Secured landfill: A site suitable for disposal of all wastes, including liquid and/or solid hazardous wastes. The site must allow no discharge of these materials or their by-products to usable ground or surface waters by leaching, percolation or any other means. Another feature which may be included is inventory control on the wastes buried in the secured landfill. The prime requisite for such disposal is that the hazardous contents of the landfill be isolated from the surrounding environment. Water quality of surface and ground water must not be compromised. Air quality must also be maintained.

Landfills may be classified as:

(1) General purpose landfills;
(2) General purpose approved landfills for small volume hazardous wastes;
(3) Approved landfills for large volume hazardous wastes;
(4) General purpose secured landfill operations for small volume - extremely hazardous wastes;
(5) Secured landfill for specific wastes for intermediate or large volume extremely hazardous wastes.

It should be noted that this classification of landfills is not that of the Environmental Protection Agency.

6.6.2.1 General Purpose Landfills

It is estimated that 55 percent of concentrated hazardous wastes of the land-destined hazardous waste from the inorganic chemicals industry currently finds its way into general purpose landfill sites. General purpose landfills are characterized by their acceptance of a wide variety of wastes, including garbage and other organic materials, and by the usual absence of special containment, monitoring, and leachate treatment provisions for hazardous wastes.

The potential for environmental damage by landfilled hazardous wastes differs depending on both the composition and quantity of that waste. Many general purpose landfills will accept small quantities of hazardous wastes, particularly if they are in drums or plastic containers, but refuse large amounts. Cyanides, arsenic compounds and some heavy metal compounds are examples of such materials. On the other hand general purpose landfills are usually wary of even small amounts of beryllium and mercury compounds.

When the hazardous level is relatively low, due either to the inherent characteristic of the compound or its low concentration in the overall waste mass, even large quantities of hazardous wastes may be accepted.

6.6.2.2 General Purpose Approved Landfills

Each general purpose landfill has its own ambience - geologically, hydrologically, and environmentally. Ideally, a general purpose landfill would be located in an isolated, dry part of the country with a thick layer of impermeable soil between the waste and the water table. Such areas are plentiful in the western U.S., but not in the east. However, many existing and future landfill sites throughout the U.S. can approach ideal conditions.

The degree of approach is differentiated in this report as approved landfills and secured landfills. Secured landfills are defined and discussed in a following section.

Approved general purpose landfills are defined to meet the following criteria:

(1) The composition and volume of each hazardous waste is known and approved for site disposal by pertinent regulatory agencies.

(2) The site should be environmentally suitable for hazardous wastes.
(3) Provision is made for monitoring wells and leachate control and treatment if required.

The advantages of approved landfill sites include:

(1) Many hazardous wastes may be disposed of in a controlled and environmentally safe fashion.
(2) Selection of landfill sites and disposal technology for environmental suitability still leaves a great number of available landfill sites.
(3) Disposal costs, for both transporting the waste to the site and the landfilling itself, are kept to levels close to those for general purpose sites and still much lower than for secured landfill.

From a practical standpoint many local regulatory agencies and landfill site owners are informally practicing much of this discrimination by selective acceptance of waste materials. Sites with known high potential for surface and groundwater contamination are thereby avoided.

6.6.2.3 Approved Landfill for Large Volume Hazardous Wastes

Whenever the volume of a potentially hazardous waste is large, general purpose landfill operations are no longer appropriate. These wastes warrant, and because of their small number can be given, special attention. In the inorganic chemicals industry these large volume wastes usually come from ore residues and process by-products. Examples are chrome ore residues from sodium dichromate production and calcium fluoride-calcium sulfate residues from hydrofluoric acid production. Hazardousness for these wastes is generally of a lower level than for more concentrated and/or toxic compounds. On the basis of this selection, a rough estimate is that 5 percent of the total wastes are disposed of in this fashion. Large volume hazardous wastes normally have their own landfill site so that interaction with other wastes is not a factor. Also, since transportation costs are high, disposal is usually either on-site or within a few miles of the plant.

In view of their small number, large size, and transportation restrictions, each of these wastes can be given in-depth disposal analysis for environmental safety.

6.6.2.4 General Purpose Secured Landfills

The inorganic chemicals industry has a number of small volume wastes of extremely hazardous potential. For these wastes landfilling involves additional safeguards beyond those described for approved landfills. Criteria for these secured landfills include:

(1) The composition and volume of each extremely hazardous waste is known and approved for site disposal by pertinent regulatory agencies.
(2) The site should be geologically and hydrologically approved for extremely hazardous wastes. Included in the criteria would be a soil or soil-liner permeation rate of less than 10^{-7} cm./sec, a water table well below the lowest level of the landfill and adequate provision for diversion and control of surface water.
(3) Monitoring wells are provided.
(4) Leachate control and treatment (if required).
(5) Records of burial coordinates to avoid any chemical interactions.
(6) Registration of the landfill site for a permanent record of its location once filled.

A number of landfills which meet the physical requirements (if not all the regulatory criteria) are located around the country. California has a number of Class I impermeable landfills which accept extremely hazardous materials (51). Texas has similar sites (41). A number of low level radioactive waste landfill sites accept industrial hazardous wastes (42). In addition to the radioactive waste sites, various other private secured landfills also take extremely hazardous wastes (1) (31) (34) (37). At the present time secured landfills are scattered and not fully utilized. Part of the lack of utilization stems from the fact that the majority of the sites are in isolated western areas away from inorganic chemicals industrial centers. Another reason for the lack of utilization is the high cost as compared to other available disposal methods. The present utilization of secured landfills is estimated at 5 percent.

Relatively isolated impermeable soil conditions exist in many areas of the country. If impermeable soil is not available then clay, special concrete, asphalt, plastic and other liners and covers are available to accomplish similar containment and isolation of wastes.

Once a landfill area has been isolated fron surface and groundwater contact and leachates are being handled satisfactorily, almost any non-flammable, non-explosive and non-air polluting hazardous waste can theoretically be disposed of safely. There are a number of practical restrictions, however, to this approach:

(1) In wet climates the impervious landfills are flooded with heavy rainfall. Dumping of liquids or sludges into the landfill only accentuates the problem.
(2) Some inorganic hazardous wastes create hazards for landfill personnel and/or give air pollution problems.
(3) Chemical interactions with both other materials and the liner can cause undesirable side effects.

6.6.2.5 Factors Affecting the Use of Landfills

6.6.2.5.1 Rainfall

In southwestern U.S. the annual rainfall is significantly less than the evaporation. In the San Francisco area a net evaporation rainfall differential of four feet exists. Therefore, in these dry climates, liquid and sludge hazardous wastes can be mixed into either refuse or fill dirt without having the landfill area flooded. California private and public Class I landfill areas accept liquid hazardous wastes as allowed under State requirements. Eastern U.S. on the other hand tends to handle these liquid wastes by treatment, ponding and final discharge to surface water.

6.6.2.5.2 Personnel and Air Pollution Hazards

Some hazardous chemicals, particularly liquids and sludges, are not usually landfilled even in dry climates because of danger to landfill personnel and/or air pollution. Strong acids and caustic solutions, reactive sulfides, volatile solvents and mercaptans are examples of such materials. One hazardous waste handling company is so concerned with hydrofluoric acid exposure that it has issued special treatment cards to its waste handling personnel specific to this chemical (32).

6.6.2.5.3 Chemical Interaction

Indiscriminate dumping of hazardous chemicals into landfills leads to serious interactions. The dumping of acid sludges on top of cyanides is a classic example which has actually occurred in California and perhaps other places. Acid similarly attacks metallic sulfides and changes the solubility of heavy metal precipitates. Dumping of liquids into landfill areas is particularly prone to give such interactions because of the relative mobility of liquids in seeping throughout the wastes.

In addition to the chemical interactions between landfill components, liners can also be attacked. Many plastic materials used in liners are attacked by organic solvents, oxidizing agents and other waste components. Clay liners are attacked by a variety of chemicals and become more porous. An old construction practice is to mix clay with lime to give a sand-like soil. There have been instances in California where clay liners have failed to stop seepage of hazardous wastes such as chromates into ground water (28). It is believed that chemical impairment of the clay liner was responsible.

6.7 Safeguards used in Disposal

Most land-destined hazardous wastes from the inorganic chemicals industry are company land stored (dumped on the land, stored in steel drums or containers or on the bottom of settling ponds) or in company on-site landfills. Safeguards to avoid environmental contamination include clay or plastic pond linings, the aforementioned steel drums and chemical fixation to change hazardous sludges and liquids into solids with low leaching rates.

Off-site safeguards on the remaining estimated 10-15 percent of the hazardous wastes include a number of approaches.

6.7.1 Direct Plastic/Concrete Encapsulation

Direct encapsulation of hazardous inorganic chemicals industry wastes in concrete in 55 gallon drums is now practiced by at least one contract disposer (38). The practice is used for small quantities of containerized miscellaneous hazardous wastes. Plastic film encapsulation has been used for arsenic disposal (29) and, of course, plastic pond liner age is prevalent. At least one plastic-lined secured landfill area is also being used for inorganic chemicals hazardous waste disposal. Direct bulk plastic encapsulation of solid wastes has not been encountered. Encapsulation is used for less than 0.1 percent of the off-site waste disposal.

6.7.2 Steel Drums

Steel drums, alone or with plastic liners, not only provide some long-term containment but also are the most convenient storage and transportation for relatively small quantities of inorganic hazardous waste. As such they are used widely for hazardous wastes of approximately one ton per day or less. Drum costs rapidly mount as the volume of hazardous wastes increase much above the one ton per day range and bulk handling then becomes the preferred route for storage and transportation. A rough estimate of 10-20 percent of the off-site waste is handled in drums.

6.7.3 Clay or Asphalt Encapsulation in Bulk

In wet climates, sections of or entire landfill areas are encapsulated by adding clay or asphalt "caps" or "covers" to impervious isolation cells or landfill liners (4). The impervious cover is necessary to protect the hazardous waste from rainfall flooding. Neutralizing or pH control ingredients such as lime may also be used to encase or surround the hazardous waste to avoid solubility, decomposition or other change in the character of the waste to increase its environmental damage (30) (39).

In dry climate, there is no need to encapsulate the entire landfill since rainfall and water buildup is not a problem. Isolation cells may still be constructed, however, for specific hazardous waste containment. Perhaps 10 percent of the off-site wastes are handled this way.

6.7.4 Leachate Collection and Treatment

In wet climates particularly, both private and public landfills are paying increasing attention to leachate collection, monitoring and treatment. Landfill areas in the State of Pennsylvania are representative of those in a wet climate and leaching treatment has been initiated in some public landfill areas (40). Leachate monitoring and treatment is also practiced in an on-site inorganic chemicals plant landfill. The vast majority of the landfill operations handling hazardous wastes, however, do not have any leachate control and treatment provisions.

6.7.5 Chemical Fixation

Except for the western U.S. where many aqueous hazardous wastes are being directly landfilled or evaporated, aqueous liquids are usually handled by chemical treatment as described in this section. Hazardous sludges on the other hand are being increasingly treated either on-site (2) (9) or in collection areas (55) (56) by mixing them with inorganic chemicals and catalysts to set up the entire mass into solid structures with low leachability and good land storage or landfill characteristics. There are a number of such processes which produce solids ranging from crumbly soil-like materials to concrete to ceramic slags. There has been no reported instance of chemical fixation being used on inorganic chemicals industry wastes. These processes have been used in other industries, however, to treat inorganic chemical type wastes and will most likely be used in the inorganic chemicals industry in the near future.

6.7.6 Coordinate Records

Landfilling of hazardous wastes as discussed earlier in this section can lead to undesirable chemical interactions. A few public and private landfill operations keep records of all hazardous waste burials by location and composition. By means of this record undesirable interactions may be avoided and potentially reactive chemicals isolated from each other. One necessary corollary to coordinate record keeping is prior knowledge of hazardous wastes coming to the landfill area so that a satisfactory disposal section may be selected. Prior written requests for the specific hazardous waste disposal are already required for some public and private landfill areas.

6.8 Private Contractors and Service Organizations

Off-site treatment and disposal of land-destined hazardous wastes from the inorganic chemicals industry are most often handled by private contractors and waste service organizations. The contractors may provide both hauling and disposal services or the hauling and disposal services may be provided by two different firms. In some cases the inorganic chemical companies supply their own hauling service. A list pf private treatment and disposal contractors and waste service organization is given in Appendix B. This list is not intended to be complete but does give a good cross-section of facilities, including most of the largest and most active, involved with treatment and disposal of inorganic chemical wastes.

6.9 Contractor Treatment and Disposal Costs

The costs for contractor handling of hazardous wastes from the inorganic chemical industry may be broken down into two basic components - the cost of getting the waste to the treatment and disposal facilities and the treatment and disposal costs themselves. Depending on circumstances, either cost may dominate.

6.9.1 Transportation Costs

Transportation or hauling costs depend on many factors, individualistic with each contractor and waste situation. The most important of these factors include:

(1) Distance
(2) Type of transportation used

(3) Amount of wastes
(4) Region of the country

A constant density factor has been used for all cost calculations since almost all wastes are relatively dense materials.

Almost all hazardous wastes taken from inorganic chemicals plants are transported by trucks. This transportation may be broken down into local hauling and long distance hauling. Local hauling is defined as 75 miles (one way) or less.

6.9.1.1 Local Hauling

When distances are short more then one load may be made per day. Loading and unloading times become a major factor. Fast loading by power shovels and loaders and fast unloading by simple dumping, for example, makes it possible to haul several loads per day. On the other hand, short hauls are often made with small trucks and partial loads. The effects of these variables on transportation costs for wastes are shown in Figure 6-2. Location factors given in the following section for long distance hauling can be used for geographic adjustments. Short distance (0-2 miles) railway rates for large volume bulk wastes such as ore wastes are similar to local truck rates or approximately $1.10/metric ton ($1.00/ton).

6.9.1.2 Long Distance Hauling

Motor transportation rates obtained from Interstate Commerce Commission information (10) are given in Figure 6-3 as a function of geographic location and distance hauled. Table 6-14 summarizes the mathematical equations and adjustment factors needed to calculate motor transportation costs directly. Rail shipping costs as a function of distance and geographic location are also shown in Figure 6-3.

The present scattered locations of hazardous waste treatment and disposal facilities make it necessary to haul perhaps 1 percent of the inorganic chemicals industry wastes distances of 100 to 500 miles. Costs for hauling distances such as these range from $11 to $44 per metric ton ($10 to $40 per ton) of waste, a major portion of the overall disposal costs. The percentage of wastes requiring long distance hauling may be expected to increase as regulations become more stringent.

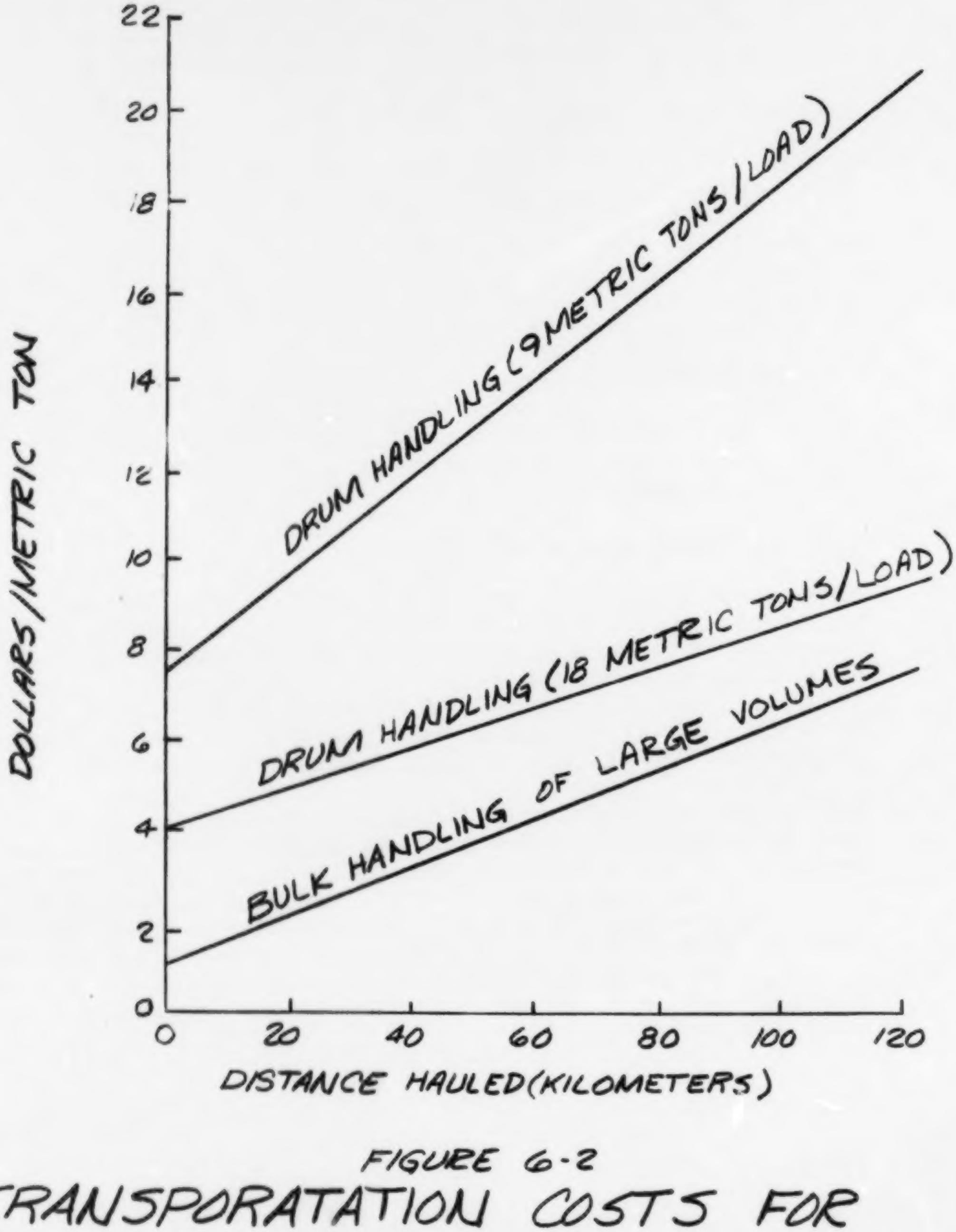
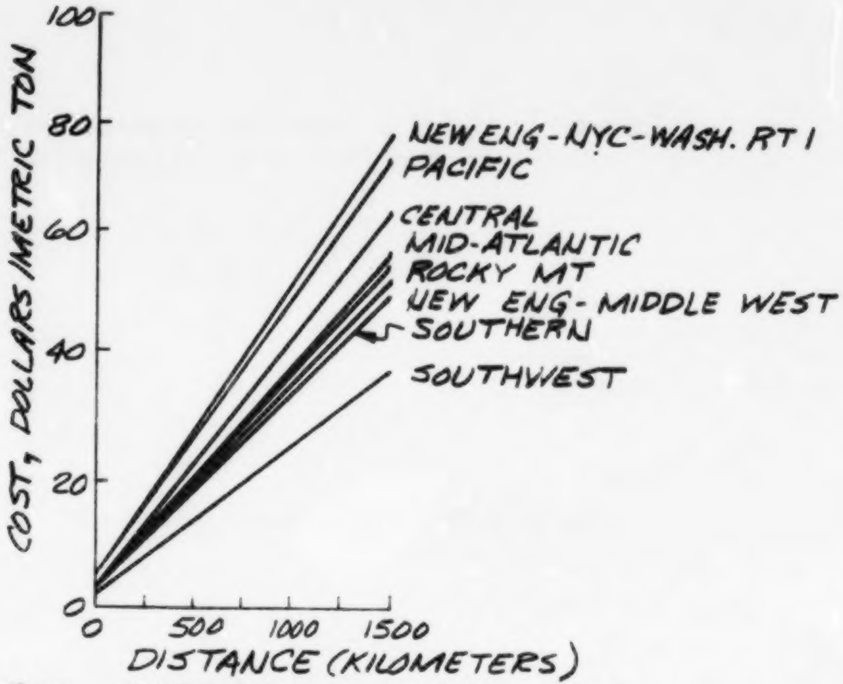
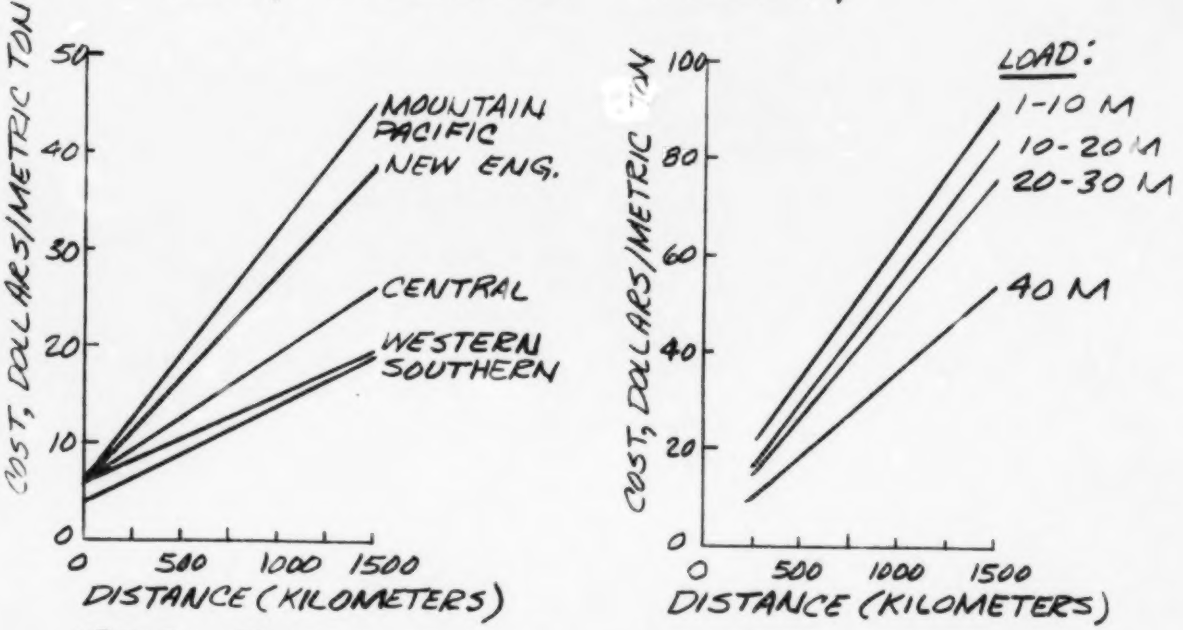


FIGURE 6-2
TRANSPORATATION COSTS FOR NORTHEASTERN U.S. LOCAL HAULING



LONG DISTANCE HAULING



1972 RAIL

1973 MOTOR

FIGURE 6-3
REGIONAL TRANSPORTATION COSTS

Table 6-14. 1973 U.S. Motor Rate Transportation Rates Est. From 1971 I.C.C. Information (Ref 10)

Terms of Equation

y = \$/ton
x = miles

Equation

$y = 6.0 + (0.0545X)$ (Region Factor) (Density Factor) (load factor)

Density Factor = 0.9

Load Factor:

1. 40,000 lbs = 1.00
2. 20m-30m lbs. = 1.42
3. 10m-20m = 1.51
4. 1m-10m = 1.74

Regional Factor:

1. New England-N.Y.C. - Wash Route 1.41
2. Pacific - 1.34
3. Central (OH, IND, IL, MI) - 1.19
4. Mid-Atlantic (NY, NJ, PA, MD, WV, DE) - 1.07
5. Rocky Mountain - 1.02
6. New England - 1.00
7. Mid-West (WI, MN, IO, MO, ND, SD, NB, KS) - 0.98
8. Southern (VA, KY, NC, SC, GA, FL, MS, AL, TN) - 0.94
9. Southwest (TX, AR, OK, LA) - 0.70

6.9.2 Treatment and Disposal Costs

With the exceptions of a few reclamation and recovery operations and a small number of chemical destructions, solid inorganic chemicals hazardous wastes are usually land stored, dumped, landfilled, or buried without treatment. Liquid and sludge wastes on the other hand are quite frequently filtered, concentrated, settled, chemically detoxified, separated and solidified before final disposal. A relatively small number of contractors are capable of carrying out these operations in any general fashion on the wide variety of liquids and sludges encountered. A number of these contractors are listed in Appendix B. Some other contractors treat and dispose of special segments of these liquid and sludge hazardous materials. Quite often solid hazardous wastes are developed in the course of liquid and sludge treatment.

6.9.2.1 Costs of Liquid and Sludge Treatments

Due to the great variety of hazardous liquid and sludge wastes from the inorganic chemicals industry, and more importantly from the inorganic chemicals users, no precise treatment and disposal costs may be developed for general situations. The competitive nature of the contract treatment and disposal business also results in a natural reluctance for contractors to pass on confidential information.

Therefore, the values given in Figure 6-4 have to be taken as ranges and approximations for any specific case. However, all the values were taken directly from major liquid waste treatment company or industrial customer numbers or literature numbers directly attributed to specific companies.

6.9.2.2 Costs for Direct Land Disposal

The lowest cost land disposal of hazardous inorganic chemicals wastes is simple dumping.

6.9.2.2.1 Dumping Costs

Dumping costs may be estimated to range from nothing to less than $1/metric ton. Zinc and chrome sludges are now being dumped in a gravel pit in quantities of several tank trucks per week at no dumping charge. Some municipal or county dumps or landfills take local wastes gratis, some of which is undoubtedly hazardous. The bulk of potentially hazardous land dumped wastes from the inorganic chemicals industry,

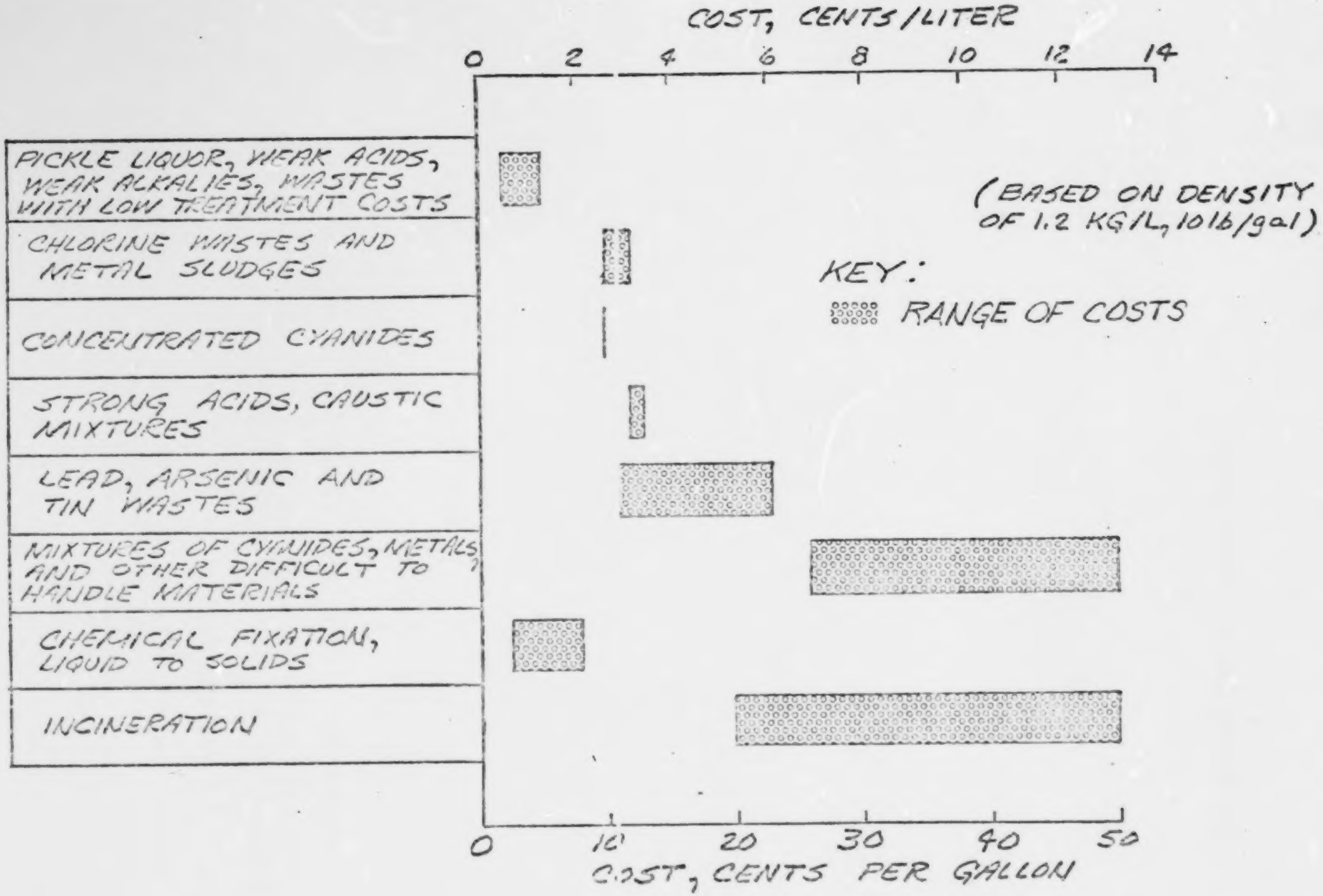


FIGURE 6-4
COSTS FOR LIQUID AND SLUDGE CONTRACT TREATMENT/DISPOSAL

however, arise from ore residues and process by-products that contain low concentrations of hazardous components.

6.9.2.2.2 Landfill Costs

Bulk Solids

Landfill costs for refuse were collected from California (several locations), New Jersey (several locations), Michigan, Illinois (several locations), New York, South Carolina and Pennsylvania. These costs range from $0-6/kkg ($0-6/ton). Hazardous inorganic chemicals wastes are undoubtedly coming in to landfills under this category. When properly identified, and disposed of according to local regulations, the average costs for easy to handle bulk materials are approximately the same, ranging from $1 to $6/metric ton ($1 to $6/ton) with an average value of approximately $2.20/metric ton ($2/ton).

Liquids

Disposal of liquids and sludges in landfills is permitted in some states and not in others. Where liquids are permitted, the disposal costs are usually higher than for bulk solids as shown in Table 6-15.

Drums

Drums of liquids, sludges, and solids, including hazardous materials, are accepted in many landfills. Table 6-16 shows some of the charges.

Segregated Burial or Secured Landfill Costs

For very hazardous materials there are a number of secured landfill or burial sites, some of which were initially established for handling radioactive wastes, which provide environmental protection above general landfill operations. These sites cost considerably more than the landfills as shown by Table 6-17 and are used only where other disposal methods are not adequate.

6.9.2.3 Ocean Disposal Contractor Costs

For inorganic chemical plants located close to the coast ocean disposal is an alternative for hazardous wastes. Table 6-18 summarizes contract costs for liquids and sludges and for small quantities of solid wastes.

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Table 6-15. Bulk Liquid and Sludge Disposal Costs*, Landfill Areas

State	¢/liter (¢/gallon)	$/metric ton ($/ton)
California, Los Angeles	0.4 (1.5)	3.30 (3)
California, Ventura	0.8 (3)	6.60 (6)
Illinois (general)	0.8 (3)	6.60 (6)
Illinois (several sites)	0.8 (3)	6.60 (6)
New Jersey	0.7-0.9 (2.5-3.5)	5.50-7.70 (5-7)
Oklahoma	0.5 (2.0)	4.40 (4)

---

*Based on 1.2 kg/liter (10 lbs/gallon)

Table 6-16. Drum Disposal Costs - Landfill Areas

State	Waste	COST $/drum*	COST $/metric ton ($/ton)
Illinois	General	3	16.50 (15)
Illinois	Heavy metals	3-5	16.50-27-50 (15-25)
Illinois	Arsenic	5	27.50 (25)
Oklahoma	Arsenic	5	27.50 (25)
Oklahoma	Cyanide	5	27.50 (25)

---

*Drum size is 208 liters (55 gallons).

Table 6-17. Segregated Burial or Secured Landfill Costs

(1)	**Bulk Materials**		
	Location	Approx. Cost $/cu m ($/ cu ft)	Approx. Cost $/kkg ($/ton
	Illinois	46-54 (1.30-1.50)	39-44 (35-40)
	Texas	46-54 (1.30-1.50)	39-44 (35-40)
	New York	54 (1.50)	44 (40)
	Idaho	36 (1.00)	30 (27)
(2)	Bulk Liquids	¢/liter (¢/gallon)	$/kkg ($/ton)
	Idaho	6.6-7.9 (25-30)	55-65 (50-60)
(3)	Drums (Solid or Liquid) Large	Number of Drums	$/kkg ($/ton)**
	Illinois	10-20	55-110 (50-100)
	Nevada	10-20	55-110 (50-100)
	Texas	10-20	55-100 (50-100)
	New York	10	55 (50)

---

*Based on 1.2 kkg/ cu m (1 ton/ cu yd)

**Based on 182 kg/drum (400 lb/drum)

NOTE: Single drums may cost as much as $50.

Table 6-18. Costs For Ocean Disposal

(1) Liquid Bulk (no treatment) - EPA Prior Approval

Volume	Cost* $/kkg ($/ton)	Cost* ¢/liter (¢/gallon)
7,570,000 liters/week (2,000,000 gallons/week)	4.40-5.50 (4.00-5.00)	0.5-0.6 (2-2½)
378,500 liters/week (100,000 gallons/week)	5.50-7.10 5.00-6.50	0.6-0.85 (2.5-3.25)
38,000 liters/week (10,000 gallons/week)	6.60-8.20 (6.00-7.50)	0.8-1.0 (6-8)
3,800 liters/week (1,000 gallons/week)	13.20-17.60 (12.00-16.00)	1.5-2.1 (6-8)

(2)

Drums, 208 liters (55 gallons), Small Lots		$/Drum**
Concrete encapsulated	Single Drum	75
Small containers	10 Drums	50-55/drum
Sodium wastes***	Single Drums	200
	20 Drum Lots	85/drum

---

*At 17 kg/liter (10 lb/gallon)

**Includes local pickup for 16-32 km (10-20 miles) radius.

***Includes riflefire drum puncture plus Coast Guard attendance.

6.9.2.4 Deep Welling Contractor Costs

Hazardous liquid wastes are disposed of by several deep well contractors in Texas and Oklahoma.

Wastes that can be injected without treatment are handled at a customer cost of $6 to $9 per ton (based on 10 pounds/gallon).

6.9.2.5 Reclamation

Although many contractors in the liquid and solid waste field do some reclamation, at least one company takes this approach for almost all wastes that they receive. Prices for disposal of these wastes through reclamation are:

Bulk Solids - $2.20 - $6.60/kkg ($2-6/ton)
Bulk Liquids - 0.5¢ - 3.2¢/liter (2¢-12¢/gallon)
Drums - 208 liters (55 gallons) - $10 each.

6.9.2.6 Contractor Pond Disposal Costs

One contractor encountered in this program stores and disposes of industrial sludge in an impervious base settling pond. Cost for this service, subtracting transportation is $1.10-1.65 per metric ton ($1.00-1.50 per ton) or 0.5¢-0.8¢ per liter (2¢-3¢ per gallon) of sludge.

7.0 COST ANALYSIS

Cost information contained in this report was assembled directly from industry, from waste treatment and disposal contractors, engineering firms, equipment suppliers, government sources, and published literature. Whenever possible, costs are based on actual installations, engineering estimates for projected facilities as supplied by contributing companies, or from waste treatment and disposal contractors quoted prices. In the absence of such information, costs estimates have been developed insofar as possible from plant-supplied costs for similar waste treatments and disposal for other plants or industries. Most of the treatment/disposal technology levels and costs developed have been submitted for comment to the specific companies and plants producing the involved chemicals. Adjustments have then been made incorporating these inputs.

Numerous cross-checks have also been made, whenever information has been available, for treatment/disposal costs from different sources, such as contract disposal companies. The estimates presented were prepared on an engineering basis, using accepted engineering format. No attempt was made to prepare estimates which would reflect impact on individual companies financial statements. Inclusion of tax considerations, product pricing, and other such factors would entail practices unique to each company, and should be recognized as beyond the scope of this report.

7.1 COST REFERENCES AND RATIONALE

7.1.1 Interest Costs and Equity Financing Charges

Capital investments involve the expenditure of money which must be financed either on borrowed money or from internal equity. Estimates for this study have been based on 10 percent cost of capital, representing a composite number for interest paid or return on investment required. This value has been established as reasonable by discussions with industry and are compatible with a recent EPA publication.(61)

7.1.2 Time Index For Costs

All cost estimates are based on mid-1973 prices and when necessary have been adjusted to this basis using the chemical engineering plant cost index. The inflationary nature of the past year makes it particularly important that this 1973 constant dollar basis be cited for any cost estimation purposes. Appendix C presents published indices which may be used to convert mid-1973 costs to December

1973. In general, costs presented herein are low by approximately 4% in terms of December 1973 dollars.

7.1.3 Useful Service Life

The useful service life of treatment and disposal equipment varies depending on the nature of the equipment and process involved, its usage pattern, maintenance care and numerous other factors. Individual companies have their own service life values based on actual experience and use these values for internal amortization. A second source of such information which, however, is based on other factors less relevant than company experience, is the Internal Revenue Service guidelines.(62)

Based on discussions with industry and condensed IRS guideline information, the following useful service life values have been used:

	Facility	Estimated Useful Service Life, Yr.
(1)	General Process Equipment	10
(2)	Incineration, Distilling and Retorting Equipment	5
(3)	Ponds, Lined and Unlined	20
(4)	Trucks, Bulldozers, Loaders and other such materials handling and transporting equipment	5

7.1.4 Depreciation

As the useful life of the treatment and disposal equipment and facilities progresses, their economic value decreases, or depreciates. At the end of their useful life, it is usually assumed that the salvage or recovery value becomes zero. IRS tax allowances, or depreciation charges, provide capital cost recovery based on either service life or accelerated write-off schedules. In effect, the straight line depreciation approach used herein is similar to a conservative depreciation approach which some companies might actually use for income tax purposes. Using a different depreciation rate would have the impact of changing the cash flow companies would actually experience based on reported expenses.

7.1.5 Capital Costs

Capital costs are defined for the purposes of this report as all front-end loaded, out-of-pocket expenditures for the provision of treatment/disposal facilities. These costs include any money for research and development necessary to establish the process, land costs when applicable, equipment, construction and installation, buildings, services, engineering, special start-up costs and contractor profits and contingencies.

When capital costs are known for a specific plant using a given treatment/disposal technology, cost adjustment to the typical plant size was made using experimental factors. Exponent values of 0.6 for process equipment, 0.8 for situations involving scale-up by use of multiple units and/or partial process equipment and partial non-volume oriented operations, and 1.0 for treatment/disposal operations that are independent of volume, at least in the range covered, were applied.

7.1.6 Annualized Capital Costs

Almost all capital costs for treatment and disposal facilities are front-end loaded; i.e., most if not all of the money is spent during the first year or two of the useful life. This present worth sum can be converted to equipment uniform annual disbursements by utilizing the Capital Recovery Factor Method:

$$\text{Uniform Annual Disbursement} = P \, \frac{i(1+i)\text{nth power}}{(1+i)\text{nth power} - 1}$$

Where P = present value (capital expenditure), i = interest rate, %/100,n = useful life in years

The capital recovery factor equation above may be rewritten as:

Uniform Annual Disbursement = P(CR - i% - n)

Where (CR - i% - n) is the Capital Recovery Factor for i% interest taken over "n" years useful life.

The capital recovery factor method is used for all annualized capital costs on this report, which, in effect, would be similar to constant annual payments on principal and interest were the capital facilities paid for through a constant payment mortgage.

7.1.7 Treatment of Land Costs

Land-destined hazardous wastes require removal of land from other economic use. The amount of land so tied up will depend on the treatment/disposal method employed and the amount of wastes involved. Although land is non-depreciable according to IRS regulations, there are instances where the market value of the land for land-destined wastes has been significantly reduced permanently, or actually become unsuitable for future use due to the nature of the stored waste. Therefore, costs estimates have assumed land values and capital recovery on the following basis:

(1) If land requirements for on-site treatment/disposal are not significant, then no cost allowance has been made.
(2) Where on-site land requirements are significant and the storage or disposal of wastes does not affect the ultimate market value of the land, cost estimates include only interest on invested money.
(3) For significant on-site land requirements where the ultimate market value and/or availability of the land has been seriously reduced, cost estimates include both capital depreciation and interest on invested money.
(4) Off-site treatment/disposal land requirements and costs are not considered directly. It is assumed that land costs are included in the overall contractor's fees along with its other expenses and profit.

In view of the extreme variability in land costs, no attempt has been made to set different land values for each plant, industry or location. Instead, a constant value of $12,350/hectare ($5000/acre) has been used throughout. Where land costs are a major portion of on-site storage/disposal costs discussions and figures have been used to demonstrate the sensitivity of costs to land value.

7.1.8 Operating Expenses

Annual costs of operating the treatment/disposal facilities include labor, supervision, materials, maintenance, taxes, insurance and power and energy. Operating costs combined with annualized capital costs give the total costs for treatment and disposal operations. No interest cost was included for operating (working) capital. Since working capital might be assumed to be one sixth to one third of annual operating costs (excluding depreciation), about 1-2% of total operating costs might be involved. This is considered to be well within the accuracy of the estimates.

a. **Labor and Supervision Costs**

Based on discussions with inorganic chemicals industry plant management personnel, the following costs are used for labor and supervisory needs.

Category	$/hour (mid-1973)
Process operators, Plant laborers	$7.50
Truck driver, Equipment operators	8.50
Supervision	10.00

The above figures include wages, fringe benefits, and plant overhead.

b. **Taxes and Insurance**

Taxes and insurance are taken as 2 percent of invested capital, excluding research and development.

c. **Other Operating Costs**

Operating costs for maintenance, materials and power and energy are variable for each individual case.

7.1.9 Rationale for "Typical Plants"

All plant costs are estimated for "typical plants" rather than for any actual plant. "Typical plants" are defined for purpose of these cost estimates as:

> the arithmetic average of production size and age for all plants, or the size and age agreed upon by a substantial fraction of the manufacturers in the subcategory producing the given chemical.

Locations are treated somewhat differently. Where pertinent, geographical descriptions of typical plants are given. In those cases where production is widely distributed, it is not given. Otherwise site location descriptions such as "industrial complex", "rural" or "urban" solitary location are given. The exclusive use of "typical plants" also allows us to maintain confidentiality of supplied information.

It should be noted here that the costs to treat and dispose of hazardous wastes at any one given plant may be considerably higher than the typical plant on a visit basis because of individual circumstances.

7.2 DEFINITION OF TECHNOLOGY LEVELS

Costs are developed for three levels of technology consistent with those defined in Phase III. These definitions redefined, with pertinent comments, are:

Level I

Technology currently employed by typical facilities; i.e. broad average present treatment and disposal practice. For most large volumed wastes two or three options are required to cover the different technologies utilized.

Level II

Best technology currently employed. Identified technology at this level must represent the soundest process from an environmental and health standpoint, currently in use in at least one (1) location. Installations must be commercial scale; pilot plant and bench scale installations are not suitable. For inorganic chemicals land-destined hazardous wastes this level may in a number of instances be similar to Level I.

Level III

Technology necessary to provide adequate health and environmental protection. Level III may be more or less sophisticated or may be identical with Level I or II Technology. At this level, identified technology may include pilot or bench scale processes providing the exact stage of development is identified. One pertinent difference between Level III Technology and Levels I and II Technology is that it is not necessary that at least one (1) location be using this technology. Technology transfers from other industries is also included.

7.3 COSTS FOR TREATMENT AND DISPOSAL OF LAND DESTINED HAZARDOUS WASTES

Treatment and disposal costs are presented below for the hazardous wastes involved in the production of individual inorganic chemicals.

7.3.1 Alkalies and Chlorine (SIC 2812)

7.3.1.1 Chlorine - Diaphragm Cell Process

Hazardous wastes from the diaphragm cell process for production of chlorine are relatively small in volume but varied in nature. These hazardous wastes include lead compounds, asbestos, and chlorinated hydrocarbons.

Because of the several approaches to handling hazardous wastes in this industry, costs have been developed for various options of treatment/disposal technology. Both lead and chlorinated hydrocarbons are rapidly diminishing in quantity and importance as the change to coated metal anodes progresses. At least 75 percent of the plants contacted are either now using coated metal anodes or plan to make the conversion in the near future. This conversion is taking place not so much for environmental reasons as for operating costs and energy savings. Asbestos will also be replaced with plastic membranes but the timing of this possible transition is uncertain.

The treatment/disposal technology situation for hazardous wastes from diaphragm cell plants is dominated by two factors:

(a) the continuing conversion to coated metal anodes is reducing the total amount of hazardous waste being generated, and,

(b) the size of the hazardous waste streams are relatively small. The brine purification sludges, which comprise the major portion of the solid wastes, are not contaminated with asbestos, lead or chlorinated hydrocarbons.

The costs for all treatment/disposal options are up to $0.30/metric ton of chlorine produced.

All indications are that the diaphragm cell chlor-alkali industry is moving in the direction of diminishing amounts of land-destined hazardous waste and that even if total elimination of these hazardous wastes is not achieved through use of plastic membranes or other process modifications the level of residual wastes will be small enough that they can be disposed of safely without any significant economic impact to the industry. Table 7-1 summarizes costs for various levels of disposal technology. The costs for the landfill and secured landfill disposals have been given as contractor disposal costs. These should be considered as bounding values.

Table 7-1. Costs For Treatment/Disposal, Diaphragm Cell Process, Alkalies and Chlorine, SIC 2812

Plant Description

450 metric tons of chlorine per day
28 years old
located in industrial complex
uses carbon anodes and asbestos separators

Hazardous Waste Stream

Form:	Sludges
Hazardous components:	0.09 kkg/day lead as metal and carbonates 0.18 kkg/day asbestos 0.2 kkg/day chlorinated hydrocarbons
Non-hazardous components:	water carbon rubble salt
Total Hazardous stream:	1.7 kkg/day (dry basis) 5.7 kkg/day (moisture included)

Level:	I		II and III
Option:	1	2	3
Investment Costs			
Land	4,000	0	0
Other	40,000	0	0
Total	44,000	0	0
Annual Costs			
Capital	500	0	0
Operating	4,000	0	0
Energy & Power	100	0	0
Contractor	3,700	7,500	50,000
Total	8,300	7,500	50,000
Cost per Metric Ton Chlorine	0.06	0.05	0.3
Overall Cost per Metric Ton of Hazardous Waste (Wet)	4.0	3.6	24.

Description of Treatment/Disposal Technical Options

(1) Pond storage of lead precipitates and asbestos, contractor burning of chlorinated hydrocarbons
(2) Landfill (off-site) for asbestos and lead sludge and burning of chlorincated hydrocarbons by contractors.
(3) Secured landfill (off-site) for asbestos, lead sludges and chlorinated hydrocarbons

7.3.1.2 Chlorine-Mercury Cell Process

Although there are small amounts of chlorinated hydrocarbons present in the hazardous wastes from this process the predominant contaminant is mercury. Wastes come from three general sources:

(a) brine purification muds containing low concentrations of mercury but often rather large in volume,
(b) process wastes - often rich in mercury content but rather low in volume. These wastes include filter sludges, vessel cleanouts, leaks and spills,
(c) water treatment precipitates - again small but concetrated in mercury content, usually as the sulfide.

Costs have been developed for several options of treatment/disposal technology for mercury-containing sludges (see Table 7-2). In addition to technology options, factors which have paramount influence on costs, the purity of the salt used and availability of secured landfill facilities, have also been costed and are shown in summary Figures 7-1.

The treatment/disposal technology costs range greatly depending on the treatment/disposal option, amount of brine impurities and availability of secured landfill facilities. For purposes of these calculations it has been assumed that secured landfill is not available on-site and has to be contracted.

Conclusions that may be drawn from the cost calculations are:

(a) For all treatment/disposal technologies it is important that the water of the mercury-containing sludges be minimized. Distillation of water in retorting operations significantly increases the fuel requirements. Contract disposal of water in secured landfill is also not desirable. Whenever possible solid contents of sludges should be at least 40-50 percent.
(b) On-site secured landfill facilities may be the most economically attractive approach. Cost calculations indicate approximately $8/ton (of waste) for on-site landfill as contrasted with $50/ton or more for contract secured landfill disposal.
(c) Off-site contracted secured landfill costs are lower or similar to retorting or extraction costs when the waste load is 40 lbs/ton or less, and the transportation distance is less than 100 miles. For long distance hauling the transportation costs become prohibitive.

Table 7-2. Costs For Treatment/Disposal, Mercury Cell Process, Alkalies and Chlorine, SIC 2812

Plant Description

250 metric tons of chlorine per day
12 years old
eastern state, in industrial complex

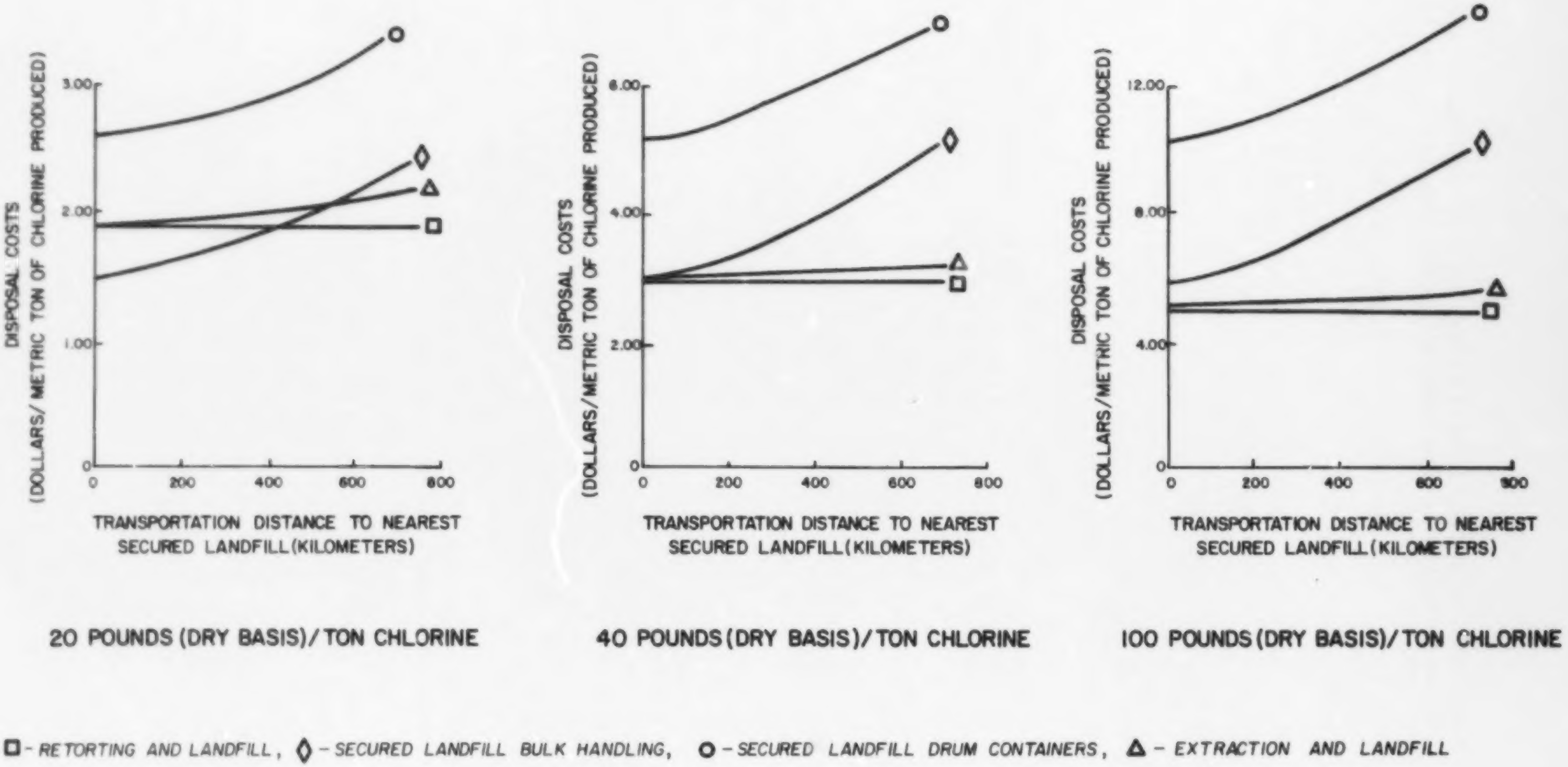
Hazardous Waste Stream

form:	sludges, muds and filter cake
hazardous components:	0.08 kkg/day chlorinated hydrocarbons 0.015 kkg/day mercury as metal, chloride and sulfide
non-hazardous components:	calcium carbonate magnesium hydroxide barium sulfate salt graphite filter aid water
total hazardous waste stream:	4.8 kkg/day (dry basis) 12 kkg/day (moisture included)

Level:	I			II	II and III	
Option:	1	2	3	4	5	6
Investment Costs						
Land	0	50,000	10,000	10,000	0	10,000
Other	15,000	350,000	30,000	470,000	0	500,000
Total	15,000	447,500	40,000	580,000	0	510,000
Annual Costs						
Capital	4,000	52,500	10,000	94,500	0	135,000
Operating	294,400	39,000	41,000	122,000	0	130,000
Energy & Power	negligible	130	2,700	6,500	0	20,000
Contractor	0	0	0	0	306,000	0
Total	298,400	91,600	53,700	222,700	306,000	285,000
Cost per Metric Ton Chlorine	3.3	1.0	0.6	3.0	3.4	2.9
Overall Cost per Metric Ton of Hazardous Waste (Wet)	68.7	20.8	12.5	62.	70.	59.

Description of Treatment/Disposal Technical Options:

(1) On-site drum storage
(2) On-site pond storage
(3) On-site landfill
(4) Chemical extraction of brine purification sludge and on-site secured landfilling of process sludges
(5) Off-site secured landfill (50 miles)
(6) Retorting of sludges and on-site landfill of residues


20 POUNDS (DRY BASIS)/TON CHLORINE

40 POUNDS (DRY BASIS)/TON CHLORINE

100 POUNDS (DRY BASIS)/TON CHLORINE

FIGURE 7-1
DISPOSAL COSTS FOR MERCURY-CONTAINING SLUDGES

(d) Contract secured landfilling is not economical at any hauling distance for waste loads greater than 75 lbs/ton.

(e) Retorting and extraction treatments which involve residues are particularly attractive for heavy waste loads, but may also be competitive at lower values.

A number of plants now follow a combination of treatment/disposal options for their wastes. One often used is to retort the high mercury content process and water treatment sludges and landstore or landfill brine sludges. Only one company is currently retorting the entire waste load. Other plants are considering this option, however, and are watching the current full waste retorting operation carefully.(23)

Brine sludge constitutes the major volume (but not amount of mercury) of hazardous wastes. If regulatory actions force brine sludge treatment or disposal in secured landfill areas, plants with large amounts of brine sludge have the options of finding new sources of salt, purifying their salt prior to possible mercury contamination, or converting to a diaphragm cell process.

7.3.1.3 Chlorine - Down's Cell Process

The only remaining land-destined hazardous wastes after treatment from the the manufacture of chlorine with co-product sodium consist of calcium-sodium sludges filtered from the product for purification purposes. Two of the five plants located near saltwater ocean barge their wastes. The other three for reasons of process confidentiality gave only sketchy descriptions of their in-process treatment technologies and the wastes involved, but recovery techniques are practiced by all three. Some report land-destined residues from the recovery process, others do not. They state that the residues are non-hazardous. The reacted cell tear-down rubble is also non-hazardous.

Table 7-3 summarizes the cost estimates for two treatment/disposal technologies. Although the economic value of the sodium product of these plants exceeds that of the chlorine product by 3-fold, for consistency with the other SIC 28121 processes, the costs per unit product have been given on a chlorine-only basis.

The Level III off-site contract treatment/disposal of the sodium-calcium sludge assumes $320/metric ton of sludge disposal costs. Safe and controlled destruction should be feasible on land, but as yet there is likely to be little demand for this service.

Table 7-3. Costs For Treatment/Disposal, Down's Cell Process, Alkalies and Chlorine, SIC 2812

Plant Description

140 metric tons of chlorine per day
sodium metal co-product
25 years old
estern state, industrial complex

Hazardous Waste Stream

form:	metallic sludge (no water) cell tear-down rubble
hazardous components:	0.9 kkg/day sodium plus calcium (elemental)-principal waste load in sludge $<$ 0.1 kkg/day sodium for residues left from cell tear-down
non-hazardous components:	negligible in sludge carbon and cell construction materials
total hazardous stream:	approx. 8-10 kkg/day contaminated rubble 0.9 kkg/day sodium-calcium sludge, where wasted

Level	I and II		III
Option	1A*	1B*	2
Investment Costs			
Land	5,000	5,000	5,000
Other	5,000	5,000	5,000
Total	10,000	10,000	10,000
Annual Costs			
Capital	1,000	1,000	1,000
Operating	4,000	34,000	34,000
Energy & Power	nil	nil	nil
Contractor	0	20,000	90,000
Total	5,000	55,000	125,000
Cost per Metric Ton Chlorine	0.1	1.1	2.4
Cost per Metric Ton of Hazardous Waste	1.4	15.	35.

Description of Treatment/Cost Options:

(1) On-site dumping and spreading of rubble contaminated with small amounts of sodium. Drumming and disposal at sea of sodium-calcium sludges by those plants having such wastes.

(2) Off-site contract land disposal of sludges. This option is a conceptualized one since no contractor presently offers this service. This estimate is based on the principal waste load of 0.9 kkg/day of sludge to cover the possibility that those disposing at sea may resort to land disposal in the future. The contaminated rubble wastes treated and disposed of as at present.

*(1A) Option (1) for those plants without sludges to waste, only contaminated rubble.
(1B) Those plants with both wastes.

7.3.2 Inorganic Pigments (SIC 2816)

7.3.2.1 Titanium Dioxide-Chloride Process

The ores from which titanium dioxide is produced contain chromium, vanadium and iron. These components are largely removed from the titanium dioxide and therefore concentrated in the wastes. Ores (and wastes) differ widely in both amount of non-titanium dioxide wastes and the composition of those wastes.

Most wastes from the chloride process are currently land disposed. Common disposal methods are on-site land dumping, off-site contract land-dumping or landfilling and deep welling. Some is ocean barged.

Approved landfills or land dumping should suffice for neutralized wastes, which are largely ore gangue and iron compounds, and small amounts of hazardous metals which are present.

In view of the vast difference in waste quantities involved with ore composition, cost estimates have been made for rutile ore (approximately 95 percent titanium dioxide) and ilmenite ore (approximately 60 percent titanium dioxide) as representative of each end of the waste load spectrum. Table 7-4 and 7-5 summarize the costs developed for wastes for each ore.

7.3.2.2 Chrome Pigments and Iron Blue

The manufacture of chrome pigments such as zinc yellow, chrome yellow, molybdate orange, chrome green, and chrome oxide green produces relatively large volumes of land-destined wastes containing lead, zinc, and chromates. Iron blue contributes complex cyanide wastes.

Chrome pigments are usually made in integrated facilities flexible to shift from one product or combination of products to another. Since iron blue is needed for manufacture of chrome green, the inclusion of iron blue manufacture with the chrome pigments is a logical one and wastes are combined.

Zinc yellow being somewhat soluble in water differs from the other chrome pigments, which are relatively insoluble, and has to be treated differently.

Some waste sludges are not now being treated prior to disposal. Attention is being paid to minimizing the amount of these sludges through at least two mechanisms:

Table 7-4. Costs For Treatment/Disposal, Chloride Process, Titanium Dioxide Pigment, SIC 2816

Plant Description

100 metric tons of pigment per day
rutile ore raw material
12 years old
located in industrial area, eastern state

Hazardous Waste Stream

form:	waste treatment sludges
hazardous components:	0.13 kkg/day chromium as $Cr(OH)_3$
non-hazardous components:	ore residues coke silica misc. metal hydroxides water
total hazardous stream:	27 kkg/day (dry basis) 110 kkg/day (moisture included)

Level	I			II and III	
Option	1	2	3	4	5
Investment Costs					
Land	5,000/yr.	0	10,000	5,000/yr	0
Other	nil	0	90,000	nil	0
Total	nil	0	100,000	nil	0
Annual Costs					
Capital	5,000	0	10,000	5,000	0
Operating	32,000	0	134,000	47,000	0
Energy & Power	nil	0	20,000	nil	0
Contractor	0	110,000	0	0	131,000
Total	37,000	110,000	164,000	53,000	131,000
Cost per Metric Ton Pigment	1	3	4.5	1.4	3.6
Cost per Metric Ton of Hazardous Waste (Wet)	0.9	2.7	4.1	1.3	3.3

Description of Treatment/Disposal Options:

(1) neutralization; precipitation of wastes and on-site storage
(2) as above, except off-site contract disposal
(3) deep-welling without treatment
(4) as (1), except approved land storage on-site
(5) as (4), except off-site

Table 7-5. Costs For Treatment/Disposal, Chloride Process, Titanium Dioxide Pigment, SIC 2816

Plant Description

100 metric tons of pigment per day
Ilmenite ore raw material
12 years old
located in industrial area, eastern state

Hazardous Waste Stream

form: waste treatment sludge

hazardous components: 0.13 kkg/day chromium as $Cr(OH)_3$

non-hazardous components: ore residues
coke
silica
misc. metal hydroxides
water

total hazardous stream: 140 kkg/day (dry basis)
560 kkg/day (moisture included)

Level	I			II and III	
Option	1	2	3	4	5
Investment Costs					
Land	25,000/yr	0	10,000	25,000/yr	0
Other	nil	0	110,000	nil	0
Total	nil	0	120,000	nil	0
Annual Costs					
Capital	25,000	0	12,000	25,000	0
Operating	140,000	0	160,000	154,000	0
Energy & Power	1,000	0	24,000	1,000	0
Contractor	0	550,000	0	0	660,000
Total	166,000	550,000	196,000	180,000	660,000
Cost per Metric Ton Pigment	4.5	15	5.4	4.9	18
Cost per Metric Ton of Hazardous Waste (Wet)	0.8	2.7	1.0	0.9	3.2

Description of Treatment/Disposal Options:

(1) neutralization; precipitation of wastes and on-site storage
(2) as above, except off-site contract disposal
(3) deep welling without treatment
(4) as (1), except approved land storage on-site
(5) as (4), except off-site

(a) Recovery during an early stage of processing so that the materials can be reused. Heavy metals and chromates are expensive and these provide some economic advantage to this approach. Two plants are now recovering these wastes completely.

(b) Maximizing the solids content of the sludges through filtration or centrifuging.

The treatment/disposal technology costs, aside from recovery, are primarily based on the availability of suitable land for disposal. This in turn depends primarily on land disposal regulations. Presently no unified set of land disposal guidelines are in existence. There are distinct movements at the state level in this direction. California, Pennsylvania, Texas and a number of other states have, are preparing, or are modifying such regulations.

Table 7-6 summarizes the costs for land disposal of sludges from the chrome pigments and iron blue industry. Land dumping is clearly the most economical. In fact, some actual land dumping disposal costs are significantly lower than the average cost estimated for the typical plant.

Simple landfilling is the next most economical disposal practice.

Secured landfill, either by off-site contract or on-site disposal is definitely more expensive. Some plants have geologically suited disposal areas on-site, most do not. In the cases where off-site contract disposal is necessary, a significant additional cost for transportation may be added. Transportation for 500 miles would approximately double the disposal costs.

Costs for secured landfill facilities vary over a wide spectrum:

Potential Costs For Secured Landfill Facilities

Type of Secured Landfill	Cost Range $/ton
Public Facilities (California, Pennsylvania etc.)	1.50-6.00*
Private (Scattered - Oklahoma, Washington, Nevada, New York, Texas, Illinois)	4.00-50.00**

Table 7-6. Costs For Treatment/Disposal, Chrome Pigments and Iron Blues, SIC 2816

Plant Description

23 metric tons of pigment per day
46 years old
northeastern state, industrial area

Hazardous Waste Stream:

form:	sludge from waste treatment
hazardous components:	0.2 kkg/day chromic hydroxide 0.6 kkg/day lead chromate 0.06 kkg/day lead hydroxide 0.1 kkg/day zinc as oxide 0.06 kkg/day iron complex cyanides
non-hazardous components:	water iron oxides and hydroxides calcium sulfate
total hazardous stream:	2.3 kkg/day (dry basis) 3 kkg/day (moisture included)

Level	I		II and III		III
Option	1	2	3	4	5
Investment Costs					
Land	0	0	0	10,000	0
Other	0	0	0	155,000	0
Total	0	0	0	165,000	0
Annual Costs					
Capital	0	0	0	28,000	0
Operating	0	0	0	28,000	0
Energy & Power	0	0	0	1,000	0
Contractor	15,000	16,000	62,000	0	62,000
Total	15,000	16,000	62,000	57,000	62,000
Cost per Metric Ton Pigment	1.7	1.9	7.5	6.9	7.5
Cost per Metric Ton of Hazardous Waste (Wet)	14.	15.	57.	52.	57.

Description of Treatment/Disposal Options:

(1) pond storage and off-site land dumping
(2) simple landfilling (contractor)
(3) secured landfilling (contractor)
(4) on-site secured landfilling
(5) contractor chemical fixation and land disposal (not proven)

* - Facilities need some modification to meet secured landfill definition but have basic potential with minor modifications.

**- Low values are usually found where favorable geological or climate conditions or fortuitous disposal facilities are available and more disposal business is needed. High values are found for specialized facilities such as radioactive materials disposal sites and where disposal conditions are difficult.

7.3.3 Industrial Inorganic Chemicals (SIC 2819)

7.3.3.1 Hydrofluoric Acid

Hydrofluoric acid is the basic chemical for the production of most fluoride chemicals.

Fluoride-containing hazardous wastes from the production of fluoride chemicals such as hydrofluoric acid, sodium silicofluoride and aluminum fluoride, and including the fluorides from phosphorus manufacture, constitute the largest volumed single category of hazardous wastes within the inorganic chemicals industry. As much as 60 percent of the total hazardous wastes from the inorganic chemicals industry contain fluorides, usually in the form of the calcium salt.

It should be pointed out, however, that calcium fluoride is only sparingly soluble in water (approximately 18 mg/liter) and that most of the calcium fluoride is present in slags or as a low percentage in major wastes such as calcium sulfate. Nevertheless, fluoride-containing wastes require attention as to both their storage and disposal. Leaching and rainwater runoff from land-destined piles of such wastes is of particular concern.

The process wastes from the manufacture of hydrofluoric acid consist of approximately 3700 kgs of calcium sulfate, calcium fluoride mixture per metric ton of acid produced. Calcium fluoride content of the waste is approximately 2 to 3 percent by weight. Although some of this waste is used in road beds, the great majority is land-dumped or landfilled. Pond storage prior to final disposal is common. Table 7-7 summarizes technology and cost levels.

Waste loads are largely determined by the process and do not vary in any significant fashion from plant to plant. The waste load is also insensitive to plant age or size.

Table 7-7. Costs For Treatment/Disposal, Hydrofluoric Acid Manufacture, SIC 2819

Plant Description

64 metric tons of hydrofluoric acid per day
18 years old
eastern state, industrial complex

Hazardous Waste Stream

form: waste treatment sludge

hazardous components: 7 kkg/day calcium fluoride

non-hazardous components: water
calcium sulfate
silica

total hazardous stream: 240 kkg/day (dry basis)
300 kkg/day (moisture included)

Level	I	II	III	
Option	1	2	3	4
Investment Costs				
Land	(5,000/yr)	0	(5,000/yr)	(10,000/yr)
Other	300,000	0	500,000	825,000
Total	300,000	0	500,000	825,000
Annual Costs				
Capital	79,000	0	133,000	218,000
Operating	91,000	0	101,000	106,000
Energy & Power	30,000	0	30,000	30,000
Contractor	0	109,000	0	0
Total	200,000	109,000	264,000	354,000
Cost per Metric Ton HF	8.6	4.7	11.3	15.2
Cost per Metric Ton of Hazardous Waste (Wet)	1.8	1.0	2.4	3.2

Description of Treatment/Disposal Options:

(1) on-site land dumping, transport by truck
(2) pond storage (ponds for water treatment needs) and contractor disposal (general)
(3) approved land dumping on-site, rainwater diversion and leachate monitoring
(4) as in (3), except secured landfill

Plant location is an important factor for several reasons:

- (a) Large amounts of disposal space are required; availability and cost of land are major factors;
- (b) Since leaching and rainfall runoff are major potential sources of environmental contamination from disposed wastes, a dry climate such as found in the western U. S. would be desirable.
- (c) Future use of the wastes for road beds, parking lots, and other useful structural purposes depends on proximity to the market. This is not a major factor today but could be for the future.

7.3.3.2 Boric Acid

Residues from boric acid production are buried in secured landfills and at a cost of $0.03 per metric ton of boric acid processed ($6 per metric ton of waste stream). Since there is only one boric acid manufacturer having a hazardous waste situation, the details of the cost breakdown are not divulged.

7.3.3.3 Aluminum Fluoride

Land-destined hazardous wastes from the manufacture of aluminum fluoride consist of aluminum fluoride, calcium fluoride, calcium sulfate and lime. Since the fluorides have only limited solubility in water they are considered to be suitable for approved landfill operations. Also, since aluminum fluoride is often produced in complexes producing other fluoride chemicals the wastes are likely to be combined with much larger quantities of similar wastes from other processes.

Low per ton costs combined with a relatively low volume of waste per ton of aluminum fluoride production gives disposal values of $0.2 to $0.6 per metric ton depending on the level of technology employed. These costs are summarized in Table 7-8.

7.3.3.4 Sodium Silicofluoride

There are three plants in the United States producing this chemical. Each uses a different waste treatment and disposal process:

Plant 1 - Has no attributable land-destined wastes since it recycles unused portions of its raw material supply back to the parent process.
Plant 2 - Deep wells all wastes.

Table 7-8. Costs For Treatment/Disposal, Aluminum Fluoride Manufacture, SIC 2819

Plant Description

145 metric tons of aluminum fluoride per day
25 years old
southeastern state, industrial complex

Hazardous Waste Stream

form: waste treatment sludge

hazardous components: 12 kkg/day calcium fluoride

non-hazardous components: calcium sulfate
hydrated lime
water

total hazardous stream: 26 kkg/day (dry basis)
33 kkg/day (moisture included)

Level	I and II		III
Option	1	2	3
Investment Costs			
Land	(1,000/yr)	0	(1,000/yr)
Other	30,000	0	120,000
Total	30,000	0	120,000
Annual Costs			
Capital	4,000	0	14,000
Operating	8,000	0	18,000
Energy & Power	small	0	small
Contractor	0	12,000	0
Total	12,000	12,000	32,000
Cost per Metric Ton AlF_3	0.2	0.2	0.6
Cost per Metric Ton of Hazardous Waste (Wet)	1.0	1.0	2.7

Description of Treatment/Disposal Options:

(1) pond storage and on-site dumping
(2) contract landfill
(3) secured landfill on-site, rainwater diversion, leachate monitoring

Plant 3 - Treats its wastes as a small portion of an overall waste stream from the chemical complex.

The small number of plants and the different waste treatment/disposal technology used at each reduces the significance of the "typical plant" for this industry segment.

Treatment and disposal of the hazardous wastes is similar to previous fluoride chemicals wastes. Deep welling of the entire waste stream without treatment costs over $8 per metric ton but by-passes expensive water treatment costs not included in the other disposal values. This cost is misleading because it can be attributed largely or wholly to waste water discharge control. Table 7-9 summarizes disposal technology and cost levels.

7.3.3.5 Chromates Manufacture (Ore Processing)

Chromate ore is the source for the basic chromate chemicals such as sodium chromate, sodium dichromate, potassium dichromate, and chromic acid. The ore, which is generally of low purity produces a large volume of gangue and land-destined solid waste. Costs for various levels and options of treatment/disposal technology for land-destined wastes from the production of chromates through ore processing are given in Table 7-10.

The basic process consists of reacting chromite ore with limestone and soda ash in kilns to produce sodium dichromate and chromate. The ore residues, along with much smaller quantities of water treatment precipitates and residual water soluble chromates in the solid wastes, are large in volume, approximately 1700-3500 kg/kkg of product. Other chromium chemicals such as chromic acid and potassium dichromate are produced in secondary operations using the sodium chromates and dichromates as raw materials. Chromic acid processes have negligible hazardous solid wastes which are handled as part of the ore processing process. Potassium dichromate process solid wastes consist primarily of sodium chloride plus a small quantity of water treatment chrome precipitates and residual water soluble chromates. Solid waste volumes for the potassium dichromate process are significantly less than for the primary ore process, but aside from the sodium chloride have similar treatment and disposal technology considerations as the land-destined solid wastes from the ore process.

Table 7-9. Costs For Treatment/Disposal, Sodium Silicofluoride Manufacture, SIC 2819

Plant Description

45 metric tons of sodium silicofluoride per day
20 years old
Florida or Texas, industrial complex

Hazardous Waste Stream (lime treatment option)

form: waste treatment sludge

hazardous components: 2.6-4.5 kkg/day calcium fluoride

non-hazardous components: silica
hydrated lime
water
salt

total waste stream: 7 kkg/day (dry basis)
23 kkg/day (moisture included) — land-dumped

Level	I and II		III
Option	deep-welling	lime treatment, wastes land-dumped	lime treatment, land-dumped collection and treatment of run-off
Investment Costs			
Land	0	(1,000/yr)	(1,000/yr)
Other	650,000	34,000	44,000
Total	650,000	34,000	44,000
Annual Costs			
Capital	105,000	4,000	7,000
Operating	35,000	5,000	6,000
Energy & Power	1,000	nil	500
Contractor	0	0	0
Total	141,000	9,000	13,500
Cost per Metric Ton Sodium Silicofluoride	8.5	0.6*	0.8*
Cost per Metric Ton of Total Hazardous Waste Stream (Wet)	17.**	1.1	1.6

*Cost for solid waste disposal only. Water treatment costs not included.

**This cost given on the same moisture content basis (70%) as the land-dumped option for comparison only. It should be realized that a pumpable slurry for deep-welling would have much more water in it.

Table 7-10. Costs For Treatment/Disposal, Chromates Manufacture, SIC 2819

Plant Description

182 metric tons of sodium dichromate per day
23 years old
North Carolina, Maryland or Texas, industrial area

Hazardous Waste Stream

form:	waste treatment muds and sludges
hazardous components:	chromium as chromic hydroxide or chromate
non-hazardous components:	water ore residues
total waste stream:	150 kkg/day (dry basis) 200 kkg/day (moisture included)

Level	I			II and III	
Option	1	2	3	4	5
Investment Costs					
Land	(annualized)	(annualized)	0	(annualized)	0
Other	700,000	3,200,000	700,000	1,020,000	500,000
Total	700,000	3,200,000	700,000	1,020,000	500,000
Annual Costs					
Capital	82,000	370,000	82,000	132,000	81,000
Operating	91,000	170,000	91,000	91,000	158,000
Energy & Power	7,000	7,000	7,000	7,000	1,000
Contractor	0	0	250,000	250,000	250,000
Total	180,000	550,000	430,000	480,000	490,000
Cost per Metric Ton of Chromate	2.7	8.4	6.5	7.3	7.4
Cost per Metric Ton of Hazardous Wastes (Wet)	2.5	7.6	6.0	6.7	6.8

Description of Treatment/Disposal Options:

(1) unlined pond storage
(2) lined pond storage
(3) unlined pond storage plus on-site or local contract landfill
(4) chemical treatment plus ponding and approved contract landfill
(5) chemical treatment plus filtration and approved contract landfill

The primary hazardous wastes from all chromate processes discussed above are water soluble chromates. To maintain water quality standards for discharge of aqueous streams the chromates are usually reduced to the less hazardous chromium hydroxides by any one of a number of chemical agents such as sulfides, sulfur dioxide, ferrous sulfate and ferrous chloride followed by alkaline precipitation. Less commonly, the soluble chromates are reduced by washing and extraction operations. The solid precipitates and ore residues are then separated from the aqueous phase by filtration or pond settling.

Once the water soluble chromates have been reduced or eliminated, the solids are sent without further treatment to land storage or landfill. These wastes, if free of appreciable water soluble chromates, contain primarily inert ore residues, soluble salts such as sodium chloride, and precipitated chromium hydroxide. As may be seen in Figure 6-1 the solubility of chromium hydroxide is 0.1 mg/liter or less between pH of 7 and 9, but increases rapidly as the media becomes more acidic or basic. For this reason land storage or landfill needs to be restricted to near neutral environments.

The treatment/disposal costs are primarily due to:

(a) treatment of the aqueous waste streams to reduce all soluble chromates to very low levels, usually determined by water quality guidelines.
(b) disposal of large amounts of ore residues from the primary ore processing process.

If soluble chromates are not removed from the land-destined solid residues, significant hazardous leachate problems result, and solid wastes must be disposed of in secured landfill areas. Removal of chromates allows disposal of the solid wastes in lower cost and more available approved landfills.

The heavy load of ore residues for the ore processing chromates process makes it mandatory that:

(a) the land disposal have low cost per ton,
(b) large disposal sites are available.

7.3.3.6 Nickel Sulfate

The only land-destined wastes from the manufacture of nickel sulfate come from purification muds and water quality treatment to remove residual nickel salts. Table 7-11 summarizes disposal technology and cost levels. On-site

Table 7-11. Costs for Treatment/Disposal, Nickel Sulfate Manufacture (SIC 2819)

Plant Description

9 metric tons of nickel sulfate per day
37 years old
northcentral state, industrial area
uses plating wastes as part of raw material

Hazardous Waste Stream

form:	waste treatment sludge
hazardous components:	0.7 kg/day nickel hydroxide
non-hazardous components:	water filter aid
total waste stream:	0.5 kkg/day (dry basis) 1 kkg/day (moisture included)

Level	I and II	III	
Option	1	2	3
Investment Costs			
Land	(annualized)	0	0
Other	10,000	0	0
Total	10,000	0	0
Annual Costs			
Capital	1,200	0	0
Operating	2,500	9,000	0
Energy & Power	0	0	0
Contractor	0	18,000	13,000
Total	3,700	27,000	13,000
Cost per Metric Ton of Nickel Sulfate	1.1	8.3	3.8
Cost per Metric Ton of Hazardous Waste (Wet)	10.	75.	36.

Description of Treatment/Control Options:

(1) on-site landfill
(2) off-site secured landfill in lined drums
(3) chemical fixation by contractor off-site (not proven)

landfilling cost estimates are approximately $1/metric ton, off-site secured landfilling $8/metric ton, and chemical fixation costs $4/metric ton.

7.3.3.7 Phosphorus

Hazardous land-destined waste components from phosphorus manufacture include phosphorus itself and fluorides.

Hazardous phosphorus land-destined wastes come from air and water treatment operations and process components.

To protect the effluent water quality it is necessary to reduce or remove the following wastes:

(a) suspended phosphorus from the phossy water,
(b) fluorides, dusts and other air pollutant components through gas scrubbing from the ore calcining and furnace vents.

There are a variety of methods used for treating the phossy water including pond settling, clarifiers, filters and centrifuges. The latter three treatment methods usually involve direct return of collected phosphorus to the process. Phosphorus settled to the bottom of ponds often is allowed to remain there indefinitely.

The fluorides removed in the scrubbers are treated with lime and also allowed to settle in ponds. Because of the large quantities of settled wastes fairly frequent pond cleaning is practiced.

Phosphorus stored in the bottom of ponds is often recovered by means of:

(a) direct mining of pure phosphorus,
(b) combinations of isolation, heating (to enable separation and handling of molten phosphorus) pumping and settling sequences for gravity separations, and
(c) distillation operations. These recovery techniques are economically feasible because of the high price for elemental phosphorus.

The solid calcium fluoride wastes from the scrubbers are usually land stored or landfilled on-site.

In addition to the phosphorus and calcium fluoride wastes there is also phosphorus containing dust from electrostatic precipitators in the process. This dust may be settled in ponds and returned partially or entirely to the process, land dumped to let the small amount of phosphorus oxidize or burned to remove residual phosphorus. Fumes and air pollution problems arise from the land dumping and the burning. Burning operations may, however, be integrated with furnace fume control facilities. At least one major producer is using this approach.

The cost for treatment/disposal technology for phosphorus land-destined wastes are summarized in Table 7-12.

Recovery of phosphorus from phossy water, either as a process operation or from the settling ponds, is an economically viable option. The high recovery value of phosphorus ($300+/ton in 1973 to perhaps twice that in mid 1974) pays for most of the recovery operation costs.

7.3.3.8 Phosphorus Pentasulfide

Phosphorus is reacted with sulfur to form phosphorus pentasulfide. Hazardous waste loads are small, both from the standpoint of production tonnage of the chemical and the waste generated per unit of product.

The wastes may be either incinerated (with proper air pollution safeguard) or placed in secured landfills. Estimated costs for either secured landfilling or incineration are $0.07/metric ton of phosphorus pentasulfide produced. (See Table 7-13).

7.3.3.9 Phosphorus Trichloride

Phosphorus is reacted with chlorine to produce phosphorus trichloride. Hazardous waste loads are even smaller than for phosphorus pentasulfide. Costs for secured landfill after treatment are of the order of $0.4/metric ton. (See Table 7-14).

7.3.4 Sample Cost Calculation

Mercury Cell Process, Alkalies and Chlorine (SIC 28121)

Basis:
- (a) 40 pounds (dry) of mercury-containing sludges per ton of chlorine produced (20 kg/kkg).
- (b) All sludges are combined and stored and disposed of in the same way (unless otherwise noted).
- (c) Size of plant is 250 metric ton/day (275 ton/day) of chlorine.

Table 7-12. Costs For Treatment/Disposal, Phosphorus Manufacture, SIC 2819

Plant Description

136 metric tons of phosphorus per day
26 years old
Florida, Tennessee, Idaho, or Montana, rural area

Hazardous Waste Stream

form:	waste treatment sludges
hazardous components:	9 kkg/day calcium fluoride 7 kkg/day phosphorus
non-hazardous components:	silica hydrated lime calcium phosphate calcium sulfate water
total waste stream:	50 kkg/day (dry basis) 100 kkg/day (moisture included)

Level	I		II and III
Option	1	2	3
Investment Costs			
Land	(annualized)	(annualized)	(annualized)
Other	150,000	110,000	805,000
Total	150,000	110,000	805,000
Annual Costs			
Capital	19,000	27,000	210,000
Operating	62,000	73,600	65,000
Energy & Power	2,000	1,000	4,000
Contractor	0	0	0
Total	83,000	104,600	280,000
Cost per Metric Ton of Phosphorus	1.7	2.1	5.6
Cost per Metric Ton of Hazardous Waste (Wet)	2.3	2.8	7.7

Description of Treatment/Control Options:

(1) on-site storage of phossy water in bottom of water-filled settling ponds. Precipitator dusts land dumped. Calciner and furnace fume scrubber wastes landfilled after lime treatment.

(2) on-site storage of phossy water in bottom of water-filled unlined settling ponds. Precipitator dusts recycled. Calciner and furnace fume scrubber wastes landfilled after lime treatment.

(3) Recovery of phosphorus wastes by distillation. Precipitator dust recycled. Calciner and furnace fume scrubber wastes put in approved landfill.

Table 7-13. Costs For Treatment/Disposal, Phosphorus Pentasulfide Manufacture, SIC 2819

Plant Description

55,000 metric tons of phosphorus pentasulfide per year
18 years old
eastern state, industrial area

Hazardous Waste Stream

form:	dry residues and dusts
hazardous components:	3 kkg/year arsenic sulfide 8 kkg/year phosphorus and phosphorus sulfides
non-hazardous components:	glassy phosphates iron sulfide
total waste stream:	110 kkg per year

Level	I, II, and III	
Option	1	2
Investment Costs		
Land	0	0
Other	0	20,000
Total	0	20,000
Annual Costs		
Capital	0	2,300
Operating	0	1,000
Energy & Power	0	500
Contractor	3,900	0
Total	3,900	3,800
Cost per Metric Ton of Phosphorus Pentasulfide	0.07	0.07
Cost per Metric Ton of Hazardous Waste	35.	35.

Description of Treatment/Control Options:

(1) contract secured landfill
(2) incineration

Table 7-14. Costs for Treatment/Disposal, Phosphorus Trichloride Manufacture (SIC 2819)

Plant Description

58,000 metric tons of phosphorus trichloride per year
10-20 years old
eastern state, industrial area

Hazardous Waste Stream

form: dry residues

hazardous components: 3 kkg/year arsenic chloride

non-hazardous components:
glassy phosphates
iron chlorides

total waste stream: 60 kkg per year

Level	I, II, and III
Option	Secured contract landfill in lined drums
Investment Costs	
Land	0
Other	15,000
Total	15,000
Annual Costs	
Capital	1,700
Operating	9,000
Energy & Power	300
Contractor	9,600
Total	20,600
Cost per Metric Ton of Phosphorus Trichloride	0.4
Cost per Metric Ton of Hazardous Waste	340.

Option 3: On-site Landfill

Level I Technology

Capital Costs

Land Requirements

Sludge volume at 40% solids (40 #/ton Cl_2 divided by .40 = 100 #/ton Cl_2)

$$= 100\ \#/\text{ton}\ Cl_2 \times 275\ \text{ton/day} \times 1\ ft^3/75\# \times 365\ \text{day/yr}$$

$$= \frac{133{,}833\ ft^3/yr}{27\ ft^3/yd^3} = 4{,}957\ \frac{yd^3}{yr}$$

Use 20 ft. depth and 75% utilization of space

= 15 ft deep

$$\frac{\text{acres}}{\text{year}} = \frac{4{,}957\ yd^3/yr}{15\ ft} \times 3\ \frac{ft}{yd} \times \frac{27\ acre}{43{,}560\ yd^2}$$

= 0.62 acre/year needed

= 0.62 acre/year x $5,000/acre = $3,000/yr

Equipment

Front end loader	$10,000 x 1/2*	= $5,000
Dump truck (10 ton)	$13,000 x 1/2*	= $6,500
Bulldozer (cat-977)	$56,000 x 1/2*	= $28,000
Total		$39,500

*The capital cost for equipment is halved because it is used only approximately 1/2 time for landfill operations.

Assume 5 year life for front end loader, truck, and bulldozer

Capital recovery factor = 0.2638 (10%, 5 years)
Uniform annual series am't = $39,500 x 0.2638
= $10,420

Operating Costs

Labor 1/2* man each at $8.50/hr on front end loader, truck, and bulldozer

= $8.50/hr x 8 hr/day x 260 day/yr x 3/2

= $26,550/yr

*1/2 man indicates that only approximately 1/2 of the actual working time is spent in landfill operations.

Supervision = 25% of labor costs = $6,630

Materials = none

Maintenance = 10% of capital
= 0.10 x $42,500
= $4,250

Insurance and taxes = 2% of capital
= 0.02 x $42,500
= $850

Energy and power

(a) bulldozer uses 30 gal. diesel fuel per day, 1/2 time or 20 hr/week

(b) truck makes one trip per day using <1 gal/day

(c) front end loader makes one trip per day using 5 gal/day

This equals 21 gal/day at $0.50/gal
= $10.50/day x 260 day/year
= $2,730/year

Monitoring = negligible

Recovered values = none

Total Operating Costs

Labor	$26,520
Supervision	6,630
Maintenance	4,250
Insurance and taxes	850
Energy	2,730
Total	$40,980

Total Annual Costs

Capital Costs	$10,420
Operating Costs	40,980
Total	$51,400

Cost Per Unit Production of Chlorine Produced:

$$\frac{\$51{,}400/\text{yr}}{250 \text{ metric ton/year x } 365 \text{ days/year}} = \$0.56/\text{metric ton chlorine}$$

8.0 REFERENCES

1. Anonymous, "New York Firm Buys Chemical Waste for Recycling," Ind. Wastes, Nov./Dec. 1973, pp. 14, 15, 27.

2. Anonymous, "Truckloads of Landfill from Waste Sludge." Chemical Week, Jan. 26, 1972. pp. 41-42.

3. Besselievre, Edward B., The Treatment of Industrial Wastes, McGraw-Hill Book Co., New York, 1968.

4. Black and Veatch, Consulting Engineers, "Process Design Manual for Phosphorus Removal," U.S. EPA Program 17010 GNP Contract 14-12-936, October 1971.

5. Census of Manufactures (1972), U.S. Department of Commerce, Bureau of Census, Mc72 (P)-28A-1, Alkalies and Chlorine, November 1973.

6. Census of Manufactures (1972), U.S. Department of Commerce, Bureau of the Census, Mc72 (P)-28A-2, Industrial Gases, March 1974.

7. Census of Manufactures (1972), U.S. Department of Commerce, Bureau of the Census, Mc72 (P)-28A-3, Inorganic Pigments, March 1974.

8. Census of Manufactures (1972), U.S. Department of Commerce, Bureau of the Census, Mc72 (P)-28A-4, Industrial Inorganic Chemicals, N.E.C., December 1973.

9. Connor, J. R. "Ultimate Liquid Waste Disposal Methods." Plant Engineering. October 19, 1972.

10. "Cost of Transporting Freight by Class I and Class II Motor Common Carriers of General Commodities." (For the year 1971) Interstate Commerce Commission, Bureau of Accounts - Statement No. 2C1-71, Washington, D. C., July 1973.

11. "Current Industrial Reports - Inorganic Chemicals, 1971," Bureau of the Census, U.S. Department of Commerce, Series: M28A(71)-14, October 1972.

12. "Development Document for Proposed Effluent Limitations Guidelines - Copper, Nickel, Chromium and Zinc, Segment of the Electroplating Point Source Category," EPA-440/1-73-003, August 1973, EPA, Washington, D. C. 20460.

13. "Development Document for Proposed Effluent Guidelines for the Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category," EPA Contract No. 68-01-1513, December 1973, Washington, D. C.

14. Encyclopedia of Chemical Technology, 3rd ed., R. Kirk and D.F. Othmer, eds., McGraw-Hill Book Company, New York, 1965.

15. Environmental Protection Technology Series, Report No. EPA-R2-73-269 (June, 1973) "Treatment of Complex Cyanide Compounds For Reuse or Disposal." Office of Research and Monitoring, U.S. Environmental Protection Agency, Washington, D. C.

16. Fairall, J.M., Marshall, L.S., Rhines, C.E., "Guide for Conducting an Industrial Waste Survey," Draft only, U.S.

17. Faith, W.L., Keyes, D.B., and Clark, R.L., Industrial Chemicals, 3rd ed., John Wiley and Sons, Inc., New York, 1965.

18. Gurnham, C. Fred, Industrial Wastewater Control, Academic Press, New York, 1965.

19. "Industrial Waste Study of Inorganic Chemicals, Alkalies and Chlorine," General Technologies Corp., Reston, Va. EPA Contract No. 68-01-0020, July 1971.

20. Lund, Herbert F., Industrial Pollution Control Handbook, McGraw-Hill Book Co., New York, N.Y.

21. "Major Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category" EPA-440/1-74-007a, March 1974, Washington, D. C. 20460.

22. Patterson, J. and Minear, Roger A., "Wastewater Treatment Technology," 2nd ed., Report to Inst. of Envir. Cont., State of Illinois, January 1973.

23. Perry, R.A., "Mercury Recovery from Process Sludges," Chemical Engineering Progress, Vol. 70, No. 3, March 1974, pp. 73-80.

24. Perry, J.N., Chemical Engineer's Handbook, 4th ed., McGraw-Hill Book, Co., New York, 1962.

25. Peters, Max S., and Timmerhaus, Klaus D., Plant Design and Economics for Chemical Engineers, 2nd ed., McGraw-Hill Book Co., New York, 1968.

26. Popper, H., Modern Cost Engineering Techniques, McGraw-Hill Book Co., New York, 1970.

27. Private communications with Mr Ray Barbour, Browning-Ferris Industries, Houston, Texas.

28. Private communications with Mr. Charles Bourns, Solid Wastes Management, EPA Region 9, San Francisco, California.

29. Private communications with Mr. R.E. Dorer, Bureau of Solid Waste and Vector Control, Department of Health, State of Virginia.

30. Private communications with Mr. Bert Fowler, Waste Management, Inc., Palos Heights, Illinois.

31. Private communications with Mr. Hardage, Industrial Hazardous Waste Disposal Site, Lindsay, Oklahoma.

32. Private communications with Mr. Vic Johnson, Industrial Tank Company, Martinez, California.

33. Private Communication with Mr. Robert Kasz of Aztec Mercury Company, Alvin, Texas.

34. Private communication with Mr. John R. Kimberly, Jr., Resource Recovery Corporation, Seattle, Washington.

35. Private communication with Mr. Kenneth Nelson, Asarco Chemical Co., New York, N.Y.

36. Private communication with Mr. G.J. Niewenhuis of Western Processing Company, Kent, Washington.

37. Private communications with Mr. Gene Rinebold, Wescon, Inc., Twin Falls, Idaho.

38. Private communications with Mr. John Shea, Safety Products and Engineering, West Quincy, Massachusetts.

39. Private communications with Mr. John Starr, SCI Services Inc., Boston, Massachusetts.

40. Private communications with Mr. Carl Stead, Montgomery County Landfill, Montgomery County, Pennsylvania.

41. Private communications with Mr. B. Steingrabber, Texas Water Quality Board.

42. Private communications with Mr. Stan Williamson, Nuclear Engineering, Inc., San Ramon, California.

43. Private communication with Dr. Rodney Wood, Sherwin-Williams Company, Coffeyville, Kansas.

44. "Program for the Management of Hazardous Wastes," Battelle EPA Contract No. 68-01-0762, July 1973. Pacific Northwest Laboratories, Richland, Washington.

45. "Rail Carload Cost Scales by Territories from the Year 1970". Statement No. 1C1-70. Bureau of Accounts, Interstate Commerce Commission, Washington, D. C., May 1973.

46. "Recommended Methods of Reduction Neutralization, Recovery, or Disposal of Hazardous Waste," TRW Systems Group, Redondo Beach, California, EPA Contract No. 68-01-0089, August 1973, Vols. 1-16.

47. "Report to Congress on Hazardous Waste Disposal," EPA, June 30, 1972, p. v.

48. Sawyer, Clair N., Chemistry for Sanitary Engineers, McGraw-Hill Book Co., New York, 1960.

49. Sax, N. Irving, Dangerous Properties of Industrial Materials, Van Nostrand Reinhold Co., New York, 1968.

50. Shreve, R.N., Chemical Process Industries, 3rd ed., McGraw-Hill Book Co., New York, 1967.

51. "Tentative Guidelines for Hazardous Waste Land Disposal Facilities". California State Department of Public Health, Jan. 1972.

52. "The Economics of Clean Water," Vol. III, Inorganic Chemicals Industry Profiles, Contract No. 14-12-592, Federal Water Pollution Control Administration, U.S. Department of the Interior, March 1970.

53. The Merck Index, 8th ed., P.G. Stecher et al, eds., Merck and Co., Inc., Rahway, N.J., 1968.

54. Unpublished Communications, Allied Chemical Corporation, Chemicals Division, Morristown, New Jersey.

55. Unpublished Communications, Calgon Corporation, Pittsburgh, Pennsylvania-Cyanide Treatment.

56. Unpublished Communications, Chemical Research Laboratories, E.I. DuPont Company-Cyanide Treatments.

57. Unpublished Communications. "Cyanide Treatment with Hydrogen Peroxide." Dr. P.R. Mucenieks, Research Laboratories, FMC Chemicals, Princeton, New Jersey.

58. Unpublished Communications, "Sulfide Treatment With Hydrogen Peroxide." Dr. P.R. Mucenieks, Research Laboratories, FMC Chemicals, Princeton, N.J.

59. Witt, Phillip A., Jr., "Disposal of Solid Wastes," *Chemical Engineering*, October, 1971, pp. 67-77.

60. Federal Register, Vol. 39, No. 164, "Hazardous Substances, Designation of and Determination of Removability (EPA)".

61. Annual Report of the Administrator of the EPA, "The Cost of Clean Air", EPA Publication 230/3-74-003, April 1974.

62. Internal Revenue Service, "Guidelines for Industry, 1973".

63. Stanford Research Institute, Chemical Information Services, *1974 Directory of Chemical Producers*, Menlo Park, California.

64. The Chlorine Institute, Inc., *North American Chlor-Alkali Industry Plants and Production Data Book*, January 1974, No. 10.

65. Kienholz, P.J. "Outlook for Chlorine-Caustic Production", *Chem. Eng. Progress*, Vol. 70, No. 3, pp. 59, 63.

66. Davis, John C., "Chlor-Alkali Producers Shift to Diaphragm Cells", *Chem. Eng.*, Feb. 18, 1974, pp. 84-87.

67. Iammartino, N.R., "Chlorine, Caustic Abuilding", *Chem. Eng.*, Feb. 18, 1974, pp. 80-82.

68. TRW Systems Group, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste," Vo. XIV, Aug. 1973, PB-224593.

69. Environmental Protection Agency, "Thermal Processing and Land Disposal of Solid Waste, Guidelines", Federal Register, Vol.39, No. 158, Part III, Aug. 14, 1974.

70. Mackey, T.S., "Alteration and Recovery of Ilmenite and Rutile", Australian Mining, Nov. 1972, pp. 18-42.

71. Office of Management and Budget, Standard Industrial Classification Manual, 1972, U.S. Government Printing Office, Stock No. 4101-0066.

9.0 GLOSSARY

Adsorption - Condensation of the atoms, ions or molecules of a gas, liquid or dissolved substance on the surface of a solid called the adsorbent. The best known examples are gas/solid and liquid/solid systems.

Air pollution - The presence in the air of one or more air contaminants in quantities injurious to human, plant, animal life, or property, or which unreasonably interferes with the comfortable enjoyment thereof.

Anode - The positive terminal of an electrical source to which electrons and negatively charged ions travel.

Ash - The solid residue left after incineration in the presence of oxygen.

Bag filter - A dry collection device for recovery of particulate matter from gas streams.

Barometric Condenser - Device, operating at barometric pressure, used to change vapor into liquid by cooling.

Biochemical oxygen demand, BOD_5 - The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. Standard test conditions include dark incubation at 20°C for a specified time (usually 5 days).

Blowdown - The minimum discharge of recirculating water for the purpose of discharging materials contained in the water, the further buildup of which would cause concentration in amounts exceeding limits established by best engineering practice.

Brine - An aqueous salt solution.

Calcination - The roasting or burning of any substance to bring about physical or chemical changes; e.g., the conversion of limestone to quicklime.

Carbonation - Treatment with carbon dioxide gas.

Catalytic converter - A unit containing a packed or fluidized bed of catalyst.

Caustic - Capable of destroying or eating away by chemical action. Applied to strong bases and characterized by the presence of hydroxyl ions in solution. Usually applied as a name for sodium hydroxide.

Centrifuge - A device having a rotating container in which centrifugal force separates substances of differing densities.

Chemical oxygen demand, COD - Its determination provides a measure of the quantity of oxygen required to oxidize the organic matter (or other oxidizable matter) in a waste sample, under specific conditions of oxidizing agents, temperature and time. The general method is applied to waste samples having an organic carbon concentration greater than 15 mg/liter.

Coke - The carbonaceous residue of the destructive distillation (carbonization) of coal or petroleum.

Condensation - Transformation from a gas to a liquid.

Conditioning - A physical and/or chemical treatment given to water used in the plant or discharged.

Conductivity, electrical - The ability of a material to conduct a quantity of electricity transferred across a unit area, per unit potential gradient per unit time. In practical terms, it is used for approximating the salinity or total dissolved solids content of water.

Cooling water - Water which is used to absorb waste heat generated in the process. Cooling water can be either contact or non-contact.

Copperas - Ferrous sulfate.

Crystallization - The formation of crystalline substances from solutions or melts.

Cyclone separator - A mechanical device which removes suspended solids from gas streams.

Demineralization - The removal from water of mineral contaminants usually present in ionized form. The methods used include ion-exchange techniques, flash distillation or electrolysis.

Dewater - Remove water from solid material by wet classification, centrifugation, filtration, or similar solid-liquid separation techniques.

Digestor - A pressure vessel or autoclave used to effect dissolution of raw materials into aqueous solutions.

Effluent - The wastewater discharged from a point source to a waterway or other body of water.

Electrolysis - Decomposition by means of an electric current; the compound is split into positive and negative ions which migrate and collect at the negative and positive electrodes.

Electrostatic precipitator - A gas cleaning device using the principle of placing an electrical charge on a solid particle which is then attracted to an oppositely-charged collector plate.

Filtrate - Liquid after passing through a filter.

Filtration - Removal of solid particles from liquid or particles from air or gas stream through a permeable membrane.

Flocculation - The combination of aggregation of suspended solid particles in such a way that they form small clumps. The term is used as a synonym for coagulation.

Flotation - A separation method for ore in which a froth created in water by a variety of reagents floats some finely crushed minerals, whereas other minerals sink.

Fluidized bed reactor - A reactor in which finely divided solids are caused to behave like fluids due to their suspension in a moving gas or liquid stream.

Gas washer (or wet scrubber) - Apparatus used to remove entrained solids and other substances from a gas stream.

Hammer mill - An impact mill consisting of a rotar, fitted with movable hammers, that is revolved rapidly in a vertical plane within a closely fitting steel casing.

Hardness - The characteristic of water generally accepted to represent the total concentration of calcium and magnesium ions, usually expressed as mg/liter calcium carbonate.

Heavy metal - One of the metal elements not belonging to the alkali or alkaline earth group. In this study, the classification includes titanium, vanadium, iron, nickel, copper, mercury, lead, cadmium, and chromium.

Ion exchange - A reversible chemical reaction between a solid and a fluid by means of which ions may be interchanged from one substance to another. The customary procedure is to pass the fluid through a bed of the solid, which is granular and porous and has a limited capcaity for exchange. The process is essentially a batch type in which the ion exchanger, upon nearing depletion, is regenerated by inexpensive salts or acid.

Kiln (rotary) - A large cylindrical mechanized type of furnace used for calcination.

Leaching - The process of extraction of a soluble component from a mixture with an insoluble component, by percolation of the mixture with a solvent.

Membrane - A thin sheet of synthetic polymer, through the apertures of which small molecules can pass, while larger ones are retained.

Milling - Mechanical treatment of materials to produce a powder, to change the size or shape of metal powder particles, or to coat one powder mixture with another.

Mother liquor - The solution from which crystals are formed.

Multi-Effect evaporator - In chemical processing installations, requiring a series of evaporations and condensations, the individual units are set up in series and the latent heat of vaporization from one unit is used to supply energy for the next. Such units are called "effects" in engineering parlance as, e.g., a triple effect evaporator.

Neutralization - The addition of acid or base to a solution in order to bring the pH to a value of 7.

Oleum or fuming sulfuric acid - A solution of sulfur trioxide in sulfuric acid.

Oxidation - A chemical change in which the oxidation state (positive valence) of an element is increased.

pH - Is a measure of the relative acidity or alkalinity of water. A pH value of 7.0 indicates a neutral condition; less than 7 indicates a predominance of acids, and greater than 7, a predominance of alkalies. There is a 10-fold increase (or decrease) from one pH unit level to the next, e.g., 10-fold increase of alkalinity from pH 8 to pH 9.

Plant effluent or discharge after treatment - The wastewater discharged from the industrial plant. In this definition, any waste treatment device (pond, trickling filter, etc.) is considered part of the industrial plant.

Precipitation - The formation of solid particles in a solution.

Pretreatment - The necessary processing given materials before they can be properly utilized in a process or treatment facility.

Process effluent or discharge - The volume of wastewater emerging from a particular use in the plant.

Process water - Water which is used in the internal plant streams from which products are ultimately recovered, or water which contacts either the raw materials or product at any time.

Reduction - A chemical change in which the oxidation state (positive valence) of an element is decreased.

Reverse osmosis - A method involving application of pressure to the surface of a saline solution forcing water from the solution to pass from the solution through a membrane which is too dense to permit passage of salt ions. Hollow nylon fibers or cellulose acetate sheets are used as membranes since their large surface areas offer more efficient separation.

Sedimentation - The falling or settling of solid particles in a liquid, as a sediment.

Settling pond - A large shallow body of water into which industrial wastewaters are discharged. Suspended solids settle from the wastewaters due to the large retention time of water in the pond.

Sintering - The agglomeration of powders at temperatures below their melting points. Sintering increases strength and density of the powders.

Slaking - The process of reacting lime with water to yield a hydrated product.

Sludge - The settled mud from a thickener clarifier. Generally, almost any flocculated, settled mass.

Slurry - A watery suspension of solid materials.

Sniff gas - The exhaust or tail gas effluent from the chlorine liquefaction and compression portion of a chlor-alkali facility.

Solute - A dissolved substance.

Solvent - A liquid used to dissolve materials.

Sublimation - The direct passage of a substance from the solid state to the gaseous state without appearing in the liquid state.

Thickener - A device or system wherein the solid contents of slurries or suspensions are increased by evaporation of part of the liquid phase, or by gravity settling and mechanical separation of the phases.

Total dissolved solids (TDS) - The total amount of dissolved solid materials present in an aqueous solution.

Total organic carbon (TOC) - A measurement of the total organic carbon content of surface waters, domestic and industrial wastes, and saline waters.

Total suspended solids (TSS) - Solid particulate matter found in wastewater streams, which, in most cases, can be minimized by filtration or settling ponds.

Turbidity - A measure of the opacity or transparency of a sediment-containing waste stream. Usually expressed in Jackson units or Formazin units which are essentially equivalent in the range below 100 units.

Vaporization - A change from a liquid to a gaseous state at elevated or normal temperatures.

Wet scrubbing - A gas cleaning system using water or some suitable liquid to entrap particulate matter, fumes, and absorbable gases.

Waste discharged - The amount (usually expressed as weight) of some residual substance which is suspended or dissolved in the plant effluent.

Waste generated (raw waste) - The amount (usually expressed as weight) of some residual substance generated by a plant process or the plant as a whole. This quantity is measured before treatment.

Water recirculation or recycling - The volume of water already used for some purpose in the plant which is returned with or without treatment to be used again in the same or another process.

Water use - The total volume of water applied to various uses in the plant. It is the sum of water recirculation and water withdrawal.

Water withdrawal or intake - The volume of fresh water removed from a surface or underground water source by plant facilities or obtained from some source external to the plant. The effluent limitations guidelines for sodium dichromate and by-product sodium sulfate plants, based on the application of the best available technology economically achievable, require no discharge of process wastewater pollutants to navigable waters.

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Antimony Compounds

A. Physical/Chemical Properties

Antimony Trioxide (Sb_2O_3)

This oxide of antimony is an amphoteric, white, odorless, polymorphic crystalline powder[4] which is slightly soluble in water (16.0 mg/liter at 15°C, 8.45 mg/liter at 25°C) and readily soluble in: warm solutions of tartaric acid, or of bitartrates; acetic acid; concentrated hydrochloric and sulfuric acids and strong alkalis.[1] Antimony trioxide sublimes in a high vacuum at 400°C; m.p. 655°C, b.p. 1425°C, d. 5.67, m.w. 291.52.[1]

Antimony Trichloride ($SbCl_3$)

Antimony trichloride (m.w. 228.13, d. 3.14, m.p. 73°C, b.p. 223.5°C)[9] exists as a colorless, transparent, crystalline hygroscopic mass which reacts vigorously with moisture generating heat and HCl gas.[3] At 0°C, antimony trichloride's saturation concentration is 6016.0 g/liter of water.[9] It is also soluble in alcohol, acetone and acids.[3] In contact with water, antimony trichloride gradually hydrolyzes to antimony oxychloride (SbOCl).[1]

B. Biological Properties

Although it has a slightly better prognosis, antimony poisoning closely parallels arsenic poisoning, except that vomiting from antimony may be more prominent, perhaps because its compounds are less readily absorbed than arsenicals.[2] Temporary EKG changes are reported in humans, and severe cardiac damage observed in animals. Trivalent antimony compounds are many times more lethal than pentavalent derivative. BAL (2, 3-dimercapto-1-propanol) appears to be effective in treating antimony poisoning, at least when it is due to trivalent forms of the metal. Tolerance to antimony is denied.[2]

Signs and symptoms of antimony poisoning in addition to the aforementioned include irritation and eczematous eruptions of the skin, inflammation of the mucous membranes of the nose and throat, metallic taste and stomatitis, gastrointestinal upset with vomiting and diarrhea, and various nervous complaints, such as irritability, sleeplessness, fatigue, dizziness, and muscular and neuralgic pains.[3]

C. Environmental Properties

As a contaminant in water and soil, the provisional limit for Sb_2O_3 is 0.05 ppm as Sb.[6] The LD_{50} for rats administered antimony trioxide orally is greater than 20 gm/kg body weight.[7]

Because of its solubility, land disposal of antimony trioxide should include adequate safeguards against leaching to surface or ground water supplies.

D. Radioactive Properties: None

Arsenic and Its Compounds

A. Physical/Chemical Properties

Elemental Arsenic (As)

Metallic-looking arsenic (a.w. 74.92, m.p. 818°C at 36 atm., d. 5.72) is a shiny silver-grey, brittle, rhombohedral crystalline solid that darkens in moist air.[1] It exists in two allotropic forms: a black, amorphous solid and a yellow, crystalline solid.[4] The yellow modification, which has no metallic properties, is obtained by sudden cooling of As vapor.[1] This yellow arsenic is converted back to the gray modification upon very short exposure to ultraviolet light.[1] Elemental arsenic can be heated to burn in air with a bluish flame, giving off an odor of garlic and dense white fumes of As_2O_3.[1] It loses its lustre on exposure to air, forming a black modification and As_2O_3.[1] Arsenic is attacked by HCl in the presence of an oxidant and it is readily soluble in nitric acid.[4]

Arsenic Trichloride ($AsCl_3$)

$AsCl_3$ (m.w. 181.28, m.p. -16°C, b.p. 130.21°C, d 2.1497)[9] occurs as a clear, almost colorless to pale yellow corrosive oily liquid or needle-like crystals.[3]

This arsenic chloride is soluble in concentrated HCl and most organic liquids[4] and is miscible with or solvent for: chloroform, carbon tetrachloride, ether, iodine, phosphorus, sulfur, alkali iodides, oils and fats.[1] $AsCl_3$ is decomposed by water to $As(OH)_3$ and HCl.[1] This chloride fumes in moist air readily, liberating hydrogen chloride.[1] It becomes saturated in water at a concentration of 2.98×10^4 mg/liter.[1]

Arsenic Pentasulfide (As_2S_5)

Arsenic pentasulfide (m.w. 544.62, sublimes and decomposes at 500°C)[9] exists as a brownish-yellow, glassy, amorphous, highly refractive mass.[1] It will react with steam or water to produce toxic and corrosive fumes; it can react vigorously with oxidizing materials.[3] It is almost insoluble in water (at 0°C, solubility 1.36 mg/liter)[9] but solubilizes readily in nitric acid, alkalies and alkali sulfides. Because of arsenic pentasulfide's amphoteric nature, its solubility increases as pH increases or decreases from pH 7. As_2S_5 decomposes to sulfur and the trisulfide when heated.[4]

Dibasic Sodium Arsenate ($Na_2HAsO_4 \cdot 7H_2O$)

Heptahydrated dibasic sodium arsenate (m.w. 311.91) is anhydrous at 100°C; at about 50°C it loses 5 water molecules (29% of total weight).[1] It is a colorless, odorless crystalline salt[5] with a mild alkaline taste which is readily soluble in water (at 0°C, 54.6 g dissolve into one liter of solution; at 100°C, solubility is 1000 g/liter)[9]; it is also soluble in glycerol, and slightly so in alcohol.[9] The aqueous solution of sodium arsenate is alkaline to litmus.[1] This salt effloresces in warm air.[1]

Arsenic Disulfide (As_2S_2)

Arsenic disulfide (m.w. 213.94, m.p. 307°C, b.p. 565°C, d. 3.5)[9] exists as deep red-brown, lustrous monoclinic crystals which are practically insoluble in water, very slightly soluble in hot CS_2 and benzene[1], but readily soluble in K_2S, $NaHCO_3$[9] and alkali hydroxides.[1] It will react with water or steam to produce toxic and flammable vapors; it can react vigorously with oxidizing materials.[3]

Arsenic Trisulfide (As_2S_3)

Arsenic trisulfide (m.w. 246.04, m.p. 300°C, b.p. 700°C, d.3.46)[9] occurs as yellow monoclinic crystals[9] or powder which change to a red form at 170°C.[4] It is insoluble in hydrochloric acid[4] but dissolves in alkaline sulfide and carbonate solutions and in nitric acid (decomposes).[1] Arsenic trichloride's solubility in water is 0.5 mg/liter at 18°C.[9] It is dangerous when heated to decomposition or in contact with acid or acid fumes because it emits highly toxic fumes of sulfur and of arsenic; it will react with water or steam to produce toxic and flammable vapors; it can react vigorously on contact with oxidizing materials.[3]

B. Biological Properties

In all cases of arsenic poisoning it is presumably the ion of arsenious acid, rather than the element itself, which is the toxic principle.[2] The in vivo conversion to arsenite explains why all chemical forms of arsenic eventually produce the same toxic syndrome. One exception is gaseous AsH_3 or arsine, which is a potent hemolylic agent, unlike other arsenic derivatives.[2]

Arsenic is notorious for its toxicity to humans. Ingestion of as little as 100 mg usually results in severe poisoning and as little as 130 mg has proved fatal.[5] Furthermore, arsenic accumulates in the body, so that small doses may become fatal in time. A single dose may require ten days for complete disappearance and this slow excretion rate is the basis for the cumulative toxic effect. Chronic arsenosis is of slow onset and may not become apparent for 2-6 years. Small eruptions occur on the hands and the soles of the feet sometimes developing into arsenical cancers. Liver and heart ailments may also supervene.[5]

Finely subdivided arsenic compounds, such as arsenic trioxide are significantly more toxic than coarsely powdered material, since appreciable amounts of the latter may be eliminated in the feces without dissolving.[6] In acute poisoning, symptoms following ingestion relate to irritation of the gastrointestinal tract: nausea, vomiting, diarrhea, which can progress to shock and death.[6] In most cases the presenting symptoms are those of severe gastritis or gastroenteritis.[2] Because the lesions are due not to local corrosion but to vascular damage from absorbed arsenic, the first symptoms may be delayed several minutes or even a few hours. Eventually a violent hemorrhagic gastroenteritis leads to profound losses of fluid and electrolytes, resulting in collapse, shock and death.[2]

Occasionally the alimentary symptoms are mild or absent, in which case the presenting complaints are usually referable to the central nervous system: headache, vertigo, muscle spasm, stupor, delirium, and sometimes mania.[2] Urinary excretion of arsenic is markedly enhanced, without damage to the excretory organs, by the administration of BAL (dimercaprol). If prompt, this treatment suppresses most signs and symptoms of acute poisoning.[2]

Several incidents have demonstrated that arsenic in water may be carcinogenic.[5] There have been several instances where cancers of the skin, and possibly the liver, have been attributed to arsenic in the domestic water supply.[5]

The extreme toxicity of arsenates towards human life can be considered the same for animal life as well.[6] Although sodium arsenate, for example, is not highly toxic to fish, towards lower forms of aquatic life the toxicity of sodium arsenate is variable.[5] The threshold concentration for immobilization of *Daphnia magna* in Lake Erie water has varied from 18-31 mg/liter as sodium arsenate (i.e. 4.3-7.5 mg/liter as arsenic). The toxic threshold for the flatworm *Polycelis nigra*, is reported to be 361 mg/liter as arsenic.[5]

C. Environmental Properties

The water quality standard for arsenic and its compounds is 0.05 mg/liter as As (DWS); a more ideal limit would be 0.01 mg/liter.[6]

Because of arsenic's toxic nature, all precautions must be taken to prevent run-off from farms and orchards into streams and rivers where the arsenate compounds can adversely affect aquatic plant and animal life.[6] Although very low concentrations of arsenates actually stimulate plant growth, the presence of excessive soluble arsenic in irrigation waters will reduce the yield of crops, the main effect appearing to be the destruction of chlorophyll in the foliage.[5]

The lead and calcium arsenates after application to plant surfaces, find their way to the ground when the plant drops its leaves or when rainfall washes them from the plant onto the ground.[6] The compounds then reside in the soil where they are not easily removed except by the equally undesirable process of leaching and run-off into nearby streams and lakes. The buildup of arsenic compounds in the soil has created the problem of soil sterilization and the inability of any type of plant to grow.[6]

One of the problems with toxic materials is their tendency to concentrate through both aquatic and terrestrial food chains.[22] Aquatic macro- and micro-flora and fauna accumulate heavy metals, such as arsenic, in body tissues in significantly greater concentrations than present in the surrounding environment. These organisms are the food source for fish and insects which retain the arsenic in the tissues of the consumed organisms. The fish and insects are consumed in turn by larger organisms; this process continues to the organisms at the top of the pyramidal food chain, such as man and large carnivorous birds and mammals. The more links in the chain, the more severe the bioaccumulation phenomenon.[22]

Because of the above discussed properties of arsenic-containing wastes, the most environmentally appropriate means of disposal is recovery and reuse. Where not feasible, burial in a secure landfill is necessary.

D. Radioactive Properties: None

Asbestos

A. Chemical/Physical Properties

"Asbestos" is a generic term for a number of fire-resistant hydrated silicates that, when crushed or processed, separate into flexible fibers made up of fibrils noted for their great tensile strength.[11] Although there are many asbestos minerals, only six are of commercial importance: chrysotile, a tubular serpentine mineral, accounts for 95% of the world's production; the others, all amphiboles, are amosite, crocidolite, anthophyllite, tremolite, and actinolite.[11] The molecular formulas of these six asbestos minerals are listed below. The asbestos minerals differ in their metallic elemental content, range of fiber diameters, flexibility or hardness, tensile strength, surface properties, and other attributes that determine their industrial uses and may affect their respirability, deposition, retention, translocation, and biologic reactivity.[11]

Serpentine asbestos is a magnesium silicate the fibers of which are strong and flexible so that spinning is possible with the longer fibers.[4] Amphibole asbestos includes various silicates of magnesium, iron, calcium, and sodium. The fibers are generally brittle and cannot be spun but are more resistant to chemicals and to heat than serpentine asbestos.[4]

Molecular Formulas of Asbestos Minerals:

Chrysolite	$Mg_3Si_2O_5(OH)_4$[6]
Anthophyllite	$(MgFe)_7\ Si_8O_{22}(OHF)_2$
Amosite	(ferroanthophyllite)
Crocidolite	
Tremolite	$Ca_2Mg_2Si_{22}(OHF)_2$
Actinolite	$Ca_2(MgFe)_5\ Si_8O_{22}(OH,F)_2$[6]

B. Biological Properties

Asbestos is toxic by inhalation of dust particles; the tolerance is 5 million particles per cubic foot of air (TLV,ACGIH recommended). Like other cases of "dust lung" diseases, asbestosis develops slowly.[8] It becomes manifest usually 20-30 years after the first exposure, often long after exposure to asbestos has completely ceased. Unexplained breathlessness on exertion and productive cough often precede the disease by many years.[8]

The essential lesion produced by asbestos dust is a diffuse fibrosis which probably begins as a "collar" about the terminal bronchioles.[3] Usually at least 4-7 years of exposure are required before a serious degree of fibrosis results. There is apparently less predisposition to tuberculosis than is the case with silicosis. Prolonged inhalation can cause cancer of the lungs, pleura and peritoneum.[3]

Exposure to asbestos without development of asbestosis has been shown to increase the risk of lung cancer.[11] Other kinds of dust in addition to asbestos most likely contribute to this development. In asbestos workers who smoke, a 90-fold increase in the incidence of lung cancer over that in non-smokers has been recorded. Some research data strongly suggests a synergism of cigarette smoking and asbestos exposure in the increased risk of lung cancer. It is not known whether this is because of reduced clearance of asbestos, transportation of cigarette-smoke carcinogens by asbestos fibers, or the promotion by one factor of cancer initiated by another. Cancer caused by asbestos localizes most often in the lower lobes of the lungs in contrast to the more common site of lung cancer in the upper lobes.[11]

An otherwise rare tumor, called mesothelioma, has been identified with asbestos.[8] Mesotheliomas usually involve the pleura but also originate in the peritoneum. This malignant tumor spreads rapidly over the whole abdominal cavity and into the lymph glands of the body. As in other kinds of lung cancer, the condition starts slowly with chest pain and breathlessness; the patients seldom survive more than a year from the time the diagnosis is established.[8]

All epidemiologic studies that appear to indicate differences in pathogenicity among types of asbestos are flawed by their lack of quantitative data on cumulative exposures, fiber characteristics, and the presence of cofactors.[11] The different types, therefore, cannot be graded as to relative risk with respect to asbestosis. Fiber size is critically important in determining respirability, deposition, retention, and clearance from the pulmonary tract and is probably an important determinant of the site and nature of biologic action. Little is known about the movement of the fibers within the human body, including their potential for entry through the gastrointestinal tract. There is evidence through that bundles of fibrils may be broken down within the body to individual fibrils.[11]

C. Environmental Properties

This material is a hazard when air-borne, and a possible hazard when water-borne in large concentrations; however, it is insoluble in water. Disposal by landfill with adequate protection against surface erosion by wind or rain is the most environmentally appropriate means of disposal.

D. Radioactive Properties: None

Barium and Its Compounds

A. Physical/Chemical Properties

Elemental Barium (Ba)

Barium (a.w. 137.34, d. 3.5, m.p. 710°C, b.p. 1500°C)[9] exists as a yellowish-white, somewhat malleable, luminous, alkaline earth metal which is easily oxidizable and hence must be kept under petroleum or some other oxygen-free liquid to exclude air.[1] This element reacts readily with water, ammonia, halogens, oxygen and most acids. It is decomposed by water or alcohol with the evolution of hydrogen.[1] Barium is pyrophoric at room temperature in powder form.[4] When heated to about 200°C in hydrogen, it reacts violently, forming BaH_2.[4]

Barium Chromate ($BaCrO_4$)

Barium chromate (m.w. 253.35, d. 4.498 at 15°C)[9] is composed of yellow, heavy, monoclinic, orthorhombic crystals[1] which are only slightly soluble in water (3.4 mg/liter at 16°C, 4.4 mg/liter at 28°C)[9], dilute acetic or chromic acids but are dissolved or decomposed by mineral acids.[1] Barium chromate crystals are combustible.[4]

B. Biological Properties

Barium

The acid-soluble barium salts (carbonate, chloride, hydroxide, nitrate, acetate, sulfide) are highly toxic, whereas the insoluble barium sulfate (used in radiography) is quite benign.[2] The LD (oral) of barium chloride can be as low as 1.0 gm but much larger doses have been tolerated. For most of the acid-soluble salts of barium, the lethal dose for adults appear to lie between 1-15 grams. Death occurs within a few hours or a few days.[2] The usual result of exposure to the sulfide, oxide and carbonate is irritation to the eyes, nose and throat, and of the skin, producing dermatitis; the salts are somewhat caustic.

Acute poisoning occurs when either of the two barium salts, barium chloride ($BaCl_2$) or barium carbonate ($BaCO_3$) is ingested.[8] Barium is rapidly transmitted to and from the bloodstream, since the mucous lining of the bowels is extremely permeable to the metal.[8] During the first 30 hours after absorption, barium is retained, especially by the muscles, after which about 20 percent is eliminated by the bowels, only about 7 percent through the urine.[8] Barium also accumulates in bones and lungs, but on the other hand, liver, kidneys, brain, heart, and hair do not retain barium.[8] Once in the bloodstream, barium acts to stimulate smooth, striated and cardiac muscle; the result is violent peristalsis, arterial hypertension, muscle twitching and disturbances in cardiac action.[2] Motor disorders include stiffness and immobility of the limbs, and sometimes of the trunk, leg cramps, twitching of facial muscles, and paralysis of the tongue and pharynx with attendant loss or impairment of speech and deglutition.[2] The central nervous system may be first stimulated and then depressed.[2] Kidney damage has been described as a late complication, probably a result of circulatory insufficiency. Because barium depolarizes cell membranes, one is led to predict a hyperkalemia rather than a depression of plasma potassium. Perhaps barium induces renal tubular lesion that results in large losses of potassium, but electrolyte analyses of urine have not been reported.[2] Although the barium metal itself can be tolerated in large doses, the toxic dose of barium chloride ranges between 0.2-0.5 gram and the lethal dose up to 2.4 grams.

The chronic phase of poisoning is an occupational disease that occurs following prolonged inhalation of barium dust.[8] The benign dust disease "baritosis" is characterized by the lungs being studded with multiple nodes which resemble snow flakes in the x-ray films. When exposure to barium ceased, the lesions clear up, but, occasionally, chronic cough and expectoration of mucous persists.[8]

Barium is present in most soils in amounts varying from a few thousandths of a percent to 1 percent.[5] It is apparently not utilized by most plants except possibly in trace quantities, and indeed it is considered to be poisonous to most plants. Brazil nuts, which contain several thousand parts per million constitute an exception. The lethal concentration limit is defined as the concentration to which the substance must be reduced before definite toxic effects disappear. Barium is concentrated by goldfish from solution by a factor of about 150.[5]

Barium Chromate

Barium chromate is highly toxic when ingested[4]; its toxic nature is due mainly to the presence of chromate in the compound. See "Chromium and Its Compounds" in this section for detailed toxicological information.

C. Environmental Properties

The water quality standard for barium is 1.0 mg/liter.[6]

D. Radioactive Properties: None

Beryllium and Its Compounds

A. Physical/Chemical Properties

Elemental Beryllium (Be)

Beryllium (a.w. 9.0122, d. 1.84, m.p. 1284-1300°C, b.p. 2970°C)[9] is a hard, brittle, light weight grey-white metal which is soluble in acids (except nitric) and alkalies.[1] The steel-like hardness often attributed to beryllium is localized in a thin film of oxide on the metal.

Beryllium is a relatively rare element, found chiefly in the mineral beryl. Although the chloride and nitrate are very soluble in water, and the sulfate moderately so, the carbonate and hydroxide are almost insoluble in water.[5]

As the whole of its domain of stability lies well below that of water, beryllium is theoretically a very base metal; it is clearly a reducing agent, and very unstable in the presence of water and aqueous solutions.[18] In the presence of acid solutions it vigorously decomposes water with the evolution of hydrogen, dissolving as beryllium ions, Be^{++}; in the presence of strongly alkaline solutions, it dissolves once again with the evolution of hydrogen, but this time gives rise

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to diberyllate ions $(Be_2O_3)^{-2}$ and beryllate ions $(BeO_2)^{-2}$.

Beryllium Hydroxide $(Be(OH)_2)$

Beryllium hydroxide (m.w. 43.03, d. 1.92)[1] exists as an amorphous white powder[4] which is decomposed to the oxide (BeO) at 138°C. It is soluble in acids and alkalis.[4] At pH 9, beryllium hydroxide reaches a saturation point, in pure water, at 1.12×10^{-4} mg/liter; as the pH decreases the solubility increases such that at pH 5, the solubility of $Be(OH)_2$ is 5.06×10^{-4} mg/liter.[18]

Beryllium Oxide (BeO)

Beryllium oxide (m.w. 25.01, d. 3.01, m.p. 2530 + 30°C, b.p. (ca) 3900°C)[9] occurs as a light, white[1] amorphous powder[4] which, when 100 percent pure, insulates electrically like a ceramic but conducts heat like a metal.[4] It is soluble in acids and alkalis.[4] Beryllium oxide solubilizes to the extent of 2.02×10^{-4} mg/liter. It is least soluble (1.60×10^{-9}) mg/liter at pH 7.[18]

Because of beryllium's amphoteric nature, compounds such as $Be(OH)_2$ and BeO and hydrated beryllium oxide $(Be_2O(OH)_2)$ have pH dependent solubilities. At pH 9, $Be_2O(OH)_2$'s solubility is 9.01×10^{-8} mg/liter whereas at pH 5 it solubilizes in pure water up to 1.46×10^{-5} mg/liter.[18] It is least soluble at pH 7 (2.53×10^{-10} mg/liter).[18]

B. Biological Properties

In acute poisoning, beryllium gives rise to a chemical inflammation of the lung tissue[8]. When exposed to concentrations of beryllium of 20-60 micrograms for about 50 days, workers in beryllium producing plants developed transient inflammation of the upper air passages, nose, pharynx, trachea, and upper bronchi, which is followed by a pneumonia-like process with fever, chills, cough, sputum, and shortness of breath. If not fatal, the disease can last up to 3 months. Even without further exposure, in about 6.3 percent of the cases it is followed by the chronic form of the disease.

Chronic berylliosis starts insidiously with progressive shortness of breath, weight loss, cough, and slight production of phlegm.[8] Occasionally, the patients have a low-grade fever and nausea. If much time elapses between exposure and the development of the disease, progressive shortness of breath is practically the sole symptom. However, if the interval between exposure and the disease is short or nonexistent, patients often develop a profound progressive emaciation. They may die within a few months. As the disease develops, granulomatous inflammation, the typical feature of beryllium poisoning, is often followed by fibrosis (scarring) of the lung tissue and by damage to the heart.

Beryllium is believed to interfere with the passage of oxygen from the alveoli to the arterial blood, a condition called "alveolar capillary block".[8] An immune mechanism is indicated by the fact that beryllium ions have been found attached to protein molecules.

Although the pulmonary effects dominate the clinical picture of berylliosis, other organs are also involved, such as the liver, spleen, kidneys, and lymph glands.[8] Beryllium compounds have the capacity to cause malignant tumors in laboratory animals, namely osteosarcoma in rabbits and carcinoma of the lungs in rats and monkeys. Whether or not patients with berylliosis are prone to the development of lung cancer has not been determined. Large doses of adrenal steroids (cortisone preparations) constitute a useful treatment for the disease.

In nutrient solution, at acid pH values, beryllium is highly toxic to plants.[5] At pH values above 11.2 however, beryllium appears to be beneficial to plants with a magnesium deficiency. Solutions containing 15-20 mg/liter of beryllium delayed germination and retarded the growth of cress and mustard seeds in solution culture.

The results of testing the toxicity of three beryllium salts toward fathead minnows and bluegills in hard and soft waters are given below:

Toxicological Responses (96 Hour TLm) of Fathead Minnows and Bluegills to be Salts[5]*

Compounds	Concentration of Beryllium in mg/l			
	Fathead Minnows		Bluegills	
	Soft	Hard	Soft	Hard
Beryllium chloride	0.15	15.0	----	----
Beryllium sulfate	0.2	11.0	1.3	12.0
Beryllium nitrate	0.15	20.0	----	----

*Concentrations expressed in terms of mg/liter Be.

These results demonstrate that beryllium is considerably more toxic in soft water than hard water.

C. Environmental Properties

The water quality standard for beryllium and its compounds is 1.0 mg/liter as Be.[6]

Detailed studies have indicated that there is no preferential uptake or concentration of beryllium or beryllium compounds from the environment by any animals or plants, including humans.[6]

D. Radioactive Properties: None

Cadmium and Its Compounds

A. Physical/Chemical Properties

Elemental Cadmium (Cd)

Cadmium (a.w. 112.4 grams, m.p. 321°C, b.p. 767°C, d. 8.6)[9] occurs as a silver-white, blue-tinged lustrous metal which oxidizes in moist air.[1] It is insoluble in water, slowly soluble in hot HCl, almost unattacked by cold H_2SO_4, but converted into sulfate by hot H_2SO_4.[1] Cadmium is readily soluble in dilute HNO_3 and in ammonium nitrate solutions. One hundred grams Hg dissolves 5.17 grams of cadmium at 18°C.[1] Solutions of cadmium yield with H_2S or Na_2S a yellow precipitate which is insoluble in excess Na_2S.[1]

In the elemental form cadmium is insoluble in water.[3] Although the chloride, nitrate, and sulfate of cadmium are highly soluble in water, the carbonate and hydroxide are virtually insoluble. Hence at high pH values, cadmium will be precipitated out.[5]

Cadmium Oxide (CdO)

CdO (m.w. 128.41, d. 8.15)[9] exists in two species; as either a dark brown infusible amorphous powder or as cubic, brown crystals.[4] Both decompose on heating at 900°C and sublime at 1559°C.[20] Cadmium oxide is soluble in dilute acids and ammonium salts.[1] Because of its amphoteric nature, its solubility increases as its pH decreases. At pH 11.3, cadmium oxide's solubility in water is 0.094 ppm as Cd^{++} while at pH 9 its saturation point is 761.0 ppm as Cd^{++}.[18]

Cadmium Hydroxide ($Cd(OH)_2$)

Cadmium hydroxide (m.w. 146.43[1], m.p. 300°C, d. 4.79) is a white powder[4] consisting of trigonal or amorphous crystals.[3] It is soluble in ammonium hydroxide and dilute acid and virtually insoluble in water (2.6 mg/liter at 25°C[9]) and alkalis.[4] Cadmium hydroxide absorbs carbon dioxide from the air[4]; dehydration to CdO occurs at 130°C-200°C.

Cadmium Sulfate ($CdSO_4.0-7H_2O$)

Cadmium sulfate occurs in several hydrated forms in addition to an anhydrous form. Anhydrous cadmium sulfate (formula $CdSO_4$, m.w. 208.48, d. 4.69, m.p. 1000°C[3]) is a white powder of colorless, odorless rhomboidal crystals(3)(9) which is very soluble in water (755.0 g/liter at 0°C, 608.0 g/liter at 100°C) and insoluble in alcohol.[4] The properties of the hydrated forms are given below; all are very soluble in water and almost insoluble in alcohol.(4)(9)

Physical/Chemical Properties of Cadmium Sulfate Hydrates

$CdSO_4.H_2O$: m.w. 226.48, d. 3.79, transition pt. 108°C, monoclinic crystals[9]
$CdSO_4.4H_2O$: m.w. 280.48, d. 305[4]
$CdSO_4.7H_2O$: m.w. 334.57, d. 2.48, transition pt. 40°C, colorless, monoclinic crystals[9]
$3CdSO_4.8H_2O$: m.w. 769.50, d. 3.09, transition pt. 4°C, colorless, odorless monoclinic crystals, H_2O solubility at 0°C 1130.0 g/liter(1)(9)

Cadmium Nitrate ($Cd(NO_3)_2$)

Cadmium nitrate exists in two forms hydrated and anhydrous. Anhydrous cadmium nitrate (m.w. 236.41, m.p. 350°C) is a colorless compound which is very soluble in water (1090 g/liter at 0°C, 3260 g/liter at 60°C, 6820 g/liter at 100°C) and alcohol, and is soluble in ethyl acetate.[9] Cadmium nitrate tetrahydrate (formula $Cd(NO_3)_2).4H_2O$, m.w. 308.47, d. 2.455, m.p. 59.4°C, b.p. 132°C[9]) is a white substance composed of amorphous or hygroscopic needles.[4] It is very soluble in water (2150 g/liter in cold water), soluble in alcohol and ammonia and virtually insoluble in nitric acid.[4]

B. Biological Properties

Cadmium is absorbed into the human organism without regard to the amount already stored, nor does there appear to be a mechanism to maintain a constant level in blood and body fluids.[8] Of 50-60 micrograms taken into the system daily, about 2 micrograms are retained mainly in the kidney and liver, the rest is eliminated in the feces. Cadmium has no known biologic function. It is toxic to practically all systems and functions of the human and animal organism.[8] Cadmium inhibits the functions of enzymes containing the sulfhydrile (SH) groups, which are dependent on the presence of zinc, cobalt, and other metals. There is evidence that cadmium acts upon the smooth muscle of the blood vessels, either directly or indirectly through the agency of the kidneys.

The concentration and not the absolute amount determines the acute toxicity of cadmium.[14] Acute poisoning may result from the inhalation of cadmium dusts and fumes (usually CdO) and from the ingestion of cadmium salts.[2] Inhaled as a dust or aerosol, cadmium salts (including even the relatively insoluble oxide) probably have a toxicity rating of "supertoxic" (with a LD equal to or less than 5 mg/kg body weight) in man, with death from fatal pulmonary injury. When swallowed, cadmium compounds are much less lethal than when inhaled, in part because they induce vomiting and so are not retained. Although as little as 30 mg of soluble cadmium salts has produced severe toxic symptoms when ingested, death probably requires several hundred mg by the oral route. A severe gastroenteritis is the chief response to ingested cadmium, but both kidney and liver injuries may occur and the kidney disorder has killed experimental animals. In man the kidney damage appears to be secondary to the appearance of a low molecular weight protein in the urine. Cadmium produces more profound changes in urinary excretion of amino acids than do lead and mercury; urinary concentrations of hydroxyamino acids, threonine and serine are particularly elevated.[2]

Finely divided cadmium of a critical particle size is inflammable and may generate lethal fumes of cadmium oxide.[2] The inhalation of 40 mg of cadmium with the pulmonary retention of 4 mg has been estimated to be fatal in man.[2] In contrast to intoxication by ingestion of cadmium, the deleterious activities following inhalation of cadmium dust or fumes are largely limited to the lungs and respiratory mucosa; although acute renal necrosis can sometimes be precipitated by inhaled cadmium fumes.[2] Even brief exposure to high concentrations may result in pulmonary edema and necrosis of the pulmonary epithelium. Other symptoms precipitated by minor exposure include dryness of the throat, coughing, headache, a sense of constriction in the chest, shortness of breath (dyspnea) and vomiting.

A characteristic sign of chronic cadmium poisoning is a microcytic hypochromic anemia; another significant finding from a diagnostic standpoint may be the formation of a yellow ring as a part of the tooth structure in chronically exposed men.[2] A severe disabling emphysema without clinical or histological evidence of chronic bronchitis was the uniform syndrome exhibited by men chronically poisoned with cadmium fumes.[8]

With regard to the toxicity of cadmium toward fish, cadmium can disrupt energy production by the inhibition of oxygen uptake.[6] Within the cells, this disruption can occur at relatively low levels and be of such severity as to cause the deaths of fish, particularly the blue gill.[6] Because cadmium acts synergistically with other substances to increase toxicity, the lethal concentration for fish varies from 0.01-10.0 mg/liter depending on the test animal, type of water, temperature, and length of exposure.[5]

C. Environmental Properties

The water quality standard for cadmium and its compounds is 0.01 ppm.[6]

One of the problems with heavy metals is their tendency to concentrate through both aquatic and terrestrial food chains.[22] Aquatic macro- and microflora and fauna accumulate heavy metals such as cadmium in body tissues in significantly greater concentrations than present in the surrounding environment. These organisms are the food source for fish and insects which retain the cadmium in the tissues of the consumed organisms. The fish and insects are consumed in turn by larger organisms; this process continues to the organisms at the top of the pyramidal food chain, such as man and large carnivorous birds and mammals. The more links in the chain, the more severe the bioaccumulation phenomenon.

D. Radioactive Properties: None

Chlorinated Hydrocarbons

A. Physical/Chemical Properties

The chlorinated hydrocarbon waste stream to which this document relates is generated by purification of chlorine gas in the chlor-alkali industry; the overall properties of this waste are discussed below.

This dark-brown, tar-like waste is a mixture of chlorinated compounds of varying degrees of complexity which are partially polymerized. Therefore, a complete compound analysis would probably identify a very wide range of compounds from the simple compounds such as $C_2H_2Cl_4$ to very large, highly branched polymers. It is sparingly soluble in water, but soluble in chlorinated organic solvents, e.g. methylene chloride, and it is flammable.

The chlorinated hydrocarbons include a large number of chemicals with high insecticidal activities.[5] They are especially resistant to degradation to nontoxic end products, and many persist for months or years following application. Although most chlorinated hydrocarbons are sparingly soluble in water, their solubility is still greater than the 96 hour TL_m values.[5]

The physical/chemical properties of several chlorinated hydrocarbons are given below:[1]

Trichloromethane (Chloroform), ($CHCl_3$) is a highly refractive, nonflammable, heavy, very volatile, sweet-tasting liquid with a characteristic odor. At 25°C chloroform's solubility in water is 7.420 g/liter; d^{20}_{20} 1.484; b.p. 61-; f.p. -63.5°C; m.w. 119.39.

Carbon Tetrachloride (CCl_4) is a clear, colorless, nonflammable, heavy liquid (yields vapors 5.3 times heavier than air) with characteristic odor. It is miscible with alcohol, benzene, chloroform, ether, carbon disulfide, petroleum ether, and oils; d^{25}_{25} 1.589; b.p. 76.7°C. Carbon tetrachloride solubilizes to the extent of 0.7945 g/liter. It solidifies at -23°C.

Tetrachloroethane ($C_2H_2Cl_4$) is a nonflammable, heavy mobile liquid with a sweetish, suffocating, chloroform-like odor; d^{25}_{4} 1.58658; m.p. -44°C; b.p. 146.5°C. Tetrachloroethane is miscible with methanol, ethanol, benzene, ether, petroleum ether, carbon tetrachloride, chloroform and carbon disulfide. It has the highest solvent power of the chlorinated hydrocarbons. Tetrachloroethane is sparingly soluble in water; 2.86 grams dissolve in a liter.

1,1,2-Trichloroethane (vinyl trichloride), ($ClCH_2CHCl_2$) is a nonflammable liquid with a pleasant odor which is insoluble in water but miscible with alcohol, ether, and many other organic liquids; d. 1.4416; b.p. 113-114°C; solidifies at -35°C.

Perchloroethane (hexachloroethane), ($Cl_3C_2Cl_3$) is colorless crystals with a camphor-like odor; a specific gravity of 2.091; m.p. 185°C; sublimes at 185°C. Perchloroethane is soluble in alcohol and ether but insoluble in water.

B. Biological Properties

A summary of the levels of several chlorinated hydrocarbons that produced minimal toxicity or no effects when fed chronically to dogs and rats is given in Table 1.[14] Limits for chlorinated hydrocarbons in drinking water have been calculated primarily on the basis of the extrapolated human intake that would be equivalent to that causing minimal toxic effects in mammals (rats and dogs). To determine a safe exposure level for man, conventionally a factor of 0.1 is applied to human data where no effects have been observed; whereas a factor of 0.01 is applied to animal data when adequate human data are available for corroboration. A factor of 1/500 is generally used on animal data when no adequate and comparable human data are available.[14]

Regardless of how they enter organisms, chlorinated hydrocarbons cause symptoms of poisoning that are similar but differ in severity.[11] The severity is related to concentration of the chlorinated hydrocarbon in the nervous system, primarily in the brain. Mild intoxication causes headaches, dizziness, gastrointestinal disturbances, numbness and weakness of the extremities, apprehension and hyperirritability. In severe cases, there are muscular fasciculations spreading from the head to the extremities, followed eventually by spasm involving entire muscle groups, leading in some cases to convulsions and death.

The substitution of a chlorine atom for a hydrogen greatly increases the anaesthetic action of a member of the aliphatic hydrocarbon series.[6] In addition, the chlorine derivative is usually less specific in its action and may affect other tissues of the body in addition to those of the central nervous system; in many cases, the chlorine derivative is quite toxic. For example, chloroform, in addition to its narcotic qualities, may cause liver, heart and kidney damage.

As a general rule, the unsaturated chlorine derivatives are highly narcotic but less toxic than the saturated derivatives thus causing degenerative changes in the liver and kidneys less frequently. In the saturated group, the narcotic effect is enhanced with an increase in the number of chlorine atoms. However, there is less relationship between the number of chlorine atoms present and the toxicity of the compound.

In dealing with these chlorinated hydrocarbons, it must be remembered that a toxic action may result from

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Table 1. Recommended Limits for Chlorinated Hydrocarbon Insecticides

Compound	Long-term levels with minimal or no effects					Calculated maximum safe levels from all sources of exposure			Intake from diet		Water	
	Species	ppm in diet	Reference	mg/kg body weight/day	Reference	Safety Factor (X)	mg/kg/day	mg/man/day	mg/man/day	% of Safe Level	% of Safe Level	Recommended limit (mg/l)
Aldrin	Rat	0.5	(1)	0.083	.....	1/100	0.00083	0.0581				
	Dog	1.0	(1)	0.02	.....	1/100	0.0002	0.014	0.0007	5.0	20	0.001
	Man	.....	...	0.003	(2),(3)	1/10	0.0003	0.021				
Chlordane	Rat	2.5	(1)	0.42	.....	1/500	0.00084	0.588				
	Dog	N.A.	...	N.A.	.....	.....	....	.....	T	T	5	0.003
	Man	N.A.	...	N.A.	.....	.....	....	.....				
DDT	Rat	5.0	(1)	0.83	.....	1/100	0.008	0.56				
	Dog	400.0	(1)	8.0	.....	1/100	0.08	5.6	0.021	3.4	20	0.05
	Man	.....	...	0.5	(4)	1/10	0.05	3.5				
Dieldrin	Rat	0.5	(1)	0.083	.....	1/100	0.00083	0.0581				
	Dog	1.0	(1)	0.02	.....	1/100	0.0002	0.014	0.0040	35.0	20	0.001
	Man	.....	...	0.003	(2),(3)	1/10	0.0003	0.021				
Endrin	Rat	5.0	(5)	0.83	.....	1/500	0.00166	0.1162				
	Dog	3.0	(6)	0.06	.....	1/500	0.00012	0.0084	0.00035	4.1	20	0.0005
	Man	N.A.	...	N.A.								
Heptachlor	Rat	0.5	(1)	0.083	.....	1/500	0.000168	0.1162				
	Dog	4.0	(1)	0.08	.....	1/500	0.00016	0.0112	0.00007	0.6	2	0.0001
	Man	N.A.	...	N.A.								
Heptachlor Epoxide	Rat	0.5	(1)	0.083	.....	1/500	0.000168	0.01162				
	Dog	0.5	(1)	0.01	.....	1/500	0.00002	0.0014	0.0021	150.0	5	0.0001
	Man	N.A.	...	N.A.								
Lindane	Rat	50.0	(1)	8.3	.....	1/500	0.0166	1.162				
	Dog	15.0	(1)	0.3	.....	1/500	0.0008	0.042	0.0035	8.3	20	0.005
	Man	N.A.	...	N.A.								
Methoxychlor	Rat	100.0	(1)	17.0	.....	1/100	0.17	11.9				
	Dog	4000.0	(1)	80.0	.....	1/100	0.8	56.0	T	T	20	1.0
	Man	.....	...	2.0	(7)	1/10	0.2	14.0				
Toxaphene	Rat	10.0	(1)	1.7	.....	1/500	0.0034	0.23				
	Dog	400.0	(1)	8.0	.....	1/500	0.016	1.12	T	T	2	0.005
	Man	N.A.		N.A.								

repeated exposure to concentrations which are too low to produce a narcotic effect, and which consequently are too low to give warning of danger.[6] Individual susceptibility is also important when poisoning by this group of solvents is being considered. Certain workmen may be seriously affected by concentrations that seem to have no effect on fellow employees in the same exposure.

The chlorinated hydrocarbons are also irritants to the eyes and the mucous membranes.[6] Repeated direct exposure to the skin may result in dermatitis and poses the additional danger of absorption through the skin.

In most instances, it is difficult to predict the toxicity of chlorinated aromatic hydrocarbon compounds.[6] However, in the case of most aromatic chlorine compounds, their toxicity is usually no greater, and frequently less, than that of the corresponding aromatic hydrocarbons.

C. Environmental Properties

Maximum allowable concentrations (MAC) and water quality limitations for some chlorinated aliphatic hydrocarbons which may be constituents in the waste are listed below. The major portion of the waste is expected to be much larger molecules. This type of material is generally less toxic, more resistant to decomposition and more environmentally persistent than the compounds listed below.

Maximum Allowable Concentrations and Recommended Water and Soil Limits for Selected Chlorinated Hydrocarbons[6]

Chlorinated Aliphatic Hydrocarbon	MAC (mg/l)	Contaminant in Water and Soil (mg/l)
Carbon Tetrachloride	25	1.95
Chloroform	50	6.0
1,2-Dichloropropane	75	17.5
Ethyl Chloride	1,000	130.0
Tetrachloroethane	-----	175.0
Dichloromethane	500	87.0
Trichloroethane	500	19.0
Vinyl Chloride	-----	38.5

Chlorinated hydrocarbons are generally stable, the half-life of their residues range up to 20 years; their high solubility in fat and low solubility in water enables them to penetrate into animal food products.[8] Because of their relatively high vapor pressure, chlorinated hydrocarbons have a tendency to evaporate from soils and plants and to circulate widely in the atmosphere. Their distribution does not depend on water draining from agricultural land into streams or on dumping of residues into sewers by manufacturers; most of the chemicals move via the air. When sprayed on a field, it evaporates and adheres to dust particles that carry it long distances until it is precipitated by rain or snow. Water becomes saturated with as little as 1-2 ppb. The portion that does not dissolve quickly enters organisms living in water, particularly tiny invertebrate animals. Fish, which are extraordinarily sensitive to many chlorinated hydrocarbons, feed on these animals and further concentrate chlorinated hydrocarbon compounds in their bodies. Birds feed on fish and each link in the food chain presents an increasing build-up of chemicals. Eventually, chlorinated hydrocarbons reach humans when they consume fish, birds, other animals and plants. The major mechanism of removal of chlorinated hydrocarbons and their residues from the soil is evaporation. The effectiveness of some chlorinated hydrocarbons as insecticides, as well as their long term hazard, is the result of their strong affinity for fat. In insects and other animals, chlorinated hydrocarbon insecticides affect the central nervous system causing convulsions and paralysis. In vertebrate animals they induce degeneration of the heart muscle and of the liver. In fish, they block oxygen uptake at the gills and cause death by suffocation.

D. Radioactive Properties: None

Chromium Compounds

A. Chemical/Physical Properties

Chromium Hydroxide ($Cr(OH)_3 \cdot nH_2O$)

The solubility of this amphoteric green gelatinous precipitate[4] varies significantly with pH[20]. In the presence of chloride ions, it is least soluble at pH 8.5; 2.61×10^{-11} g Cr^{+3} is present in one liter of saturated solution. At pH 9, 3.28×10^{-11} g Cr^{+3}/liter remain in solution; at pH 7, 3.28×10^{-10} g Cr^{+3}/liter remain in solution.[18] As the pH becomes more acidic the rate of solubilization increases rapidly. At pH 5 a saturated solution of $Cr(OH)_3 \cdot nH_2O$ will contain 5.2 x 10^{-1} g Cr^{+3}/liter. At pH 3, 5.2 x 10^{3} g Cr^{+3} will dissolve in a liter of water.[18]

In the absence of chloride ions chromium hydroxide is dramatically less soluble.[18] At pH 5 the saturation concentration is 2.07 x 10^{-9} g Cr^{+3}/liter; at pH 7 and 9 the saturation concentration is below 5.2 x 10^{-12} g Cr^{+3}/liter. Please note that the data for $Cr(OH)_3$ in the absence of chloride ions may be too low. There is some indication that this is theoretical data for the nonhydrated form which is non-existent.[18]

Chromium hydroxide can be decomposed to chromic oxide (Cr_2O_3) by heat.[4]

Chromic Oxide (Cr_2O_3)

The light to dark green trigonal crystals of chromic oxide (m.w. 151.99, d. 5.21, m.p. 2435°C, b.p. 4000°C)[9] turn brown on heating but revert to a green color on cooling.[1] Because of this oxide's amphoteric nature its solubility is pH-dependent. Chromic oxide is least soluble at pH 7 (1.51 x 10^{-10} g Cr^{+3}/liter) in solutions devoid of chloride ions.[20] In the absence of chloride ions, at a pH 9, a saturated solution will contain 0.0126 x 10^{-3} g Cr^{+3}/liter.[20] Acid treatment solubilizes chromic oxide at a pH of 1, its solubility is above 52 g/liter.

Chromium Chloride (II) ($CrCl_2$)

The lustrous white needles or fused fibrous mass of this chromium salt (m.w. 122.90, d. 2.878, m.p. 824°C, b.p. 1300°C)[9] are very hygroscopic.[1] Chromous chloride is stable in dry air but oxidizes rapidly if moist; it is a powerful reducing agent. Chromium chloride is very soluble in water giving a blue solution but insoluble in alcohol and ether.

Chromium Chloride (III) ($CrCl_3$)

Chromium chloride III (m.w. 158.35, d. 2.76, m.p. 1150°C, b.p.(subl) 1300°C)[9] exists in a hydrated form, namely, chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) as well as a nonhydrated form ($CrCl_3$).[1] The hydrated form has blue-gray rhombohedral, dark green triclinic or monoclinic, or light green crystals. It is very deliquescent in air. Chromium chloride hexahydrate is soluble in water (585 g/liter at 25°C)[9] with dilute aqueous solutions being violet and concentrated aqueous solutions green. It is slightly soluble in acetone, soluble in alcohol and practically insoluble in ether. This chromium salt's solubility is pH-dependent such that its solubility is greatly reduced at pH's greater than 5.[18]

Other Trivalent Chromic Salts

The nitrate and sulfate salts are readily soluble in water, but the carbonate is quite insoluble.[5] Neutralization of the soluble salts will precipitate $Cr(OH)_3 \cdot nH_2O$.

Hexavalent Chromium Salts

Of these compounds only the sodium, potassium and ammonium chromates are soluble.[5] Hexavalent chromium can be reduced to the trivalent form by heat, organic matter or reducing agents.

B. Biological Properties

Trivalent Chromium Compounds

Trivalent chromium compounds are said to be less toxic than the hexavalent chromium compounds.[6] Eczema-like skin conditions from trivalent chromium contact have been reported. The toxicology literature discusses the hexavalent compounds in considerable detail but the available literature does not distinctly describe the hazardous properties of the trivalent compounds by themselves.[6] Internally, chrome salts act as an irritant causing tissue corrosion in the gastrointestinal tract. Complaints of bad taste in the mouth, vomiting and bloody stools are often noted. In addition, the central nervous system is often involved and dilated pupils, coma, collapse, slow respirations, shock and death sometimes occur.[6] In contact with the skin, chromium metal and Cr^{+3} combine with proteins to form complexes in the superficial layers.

Hexavalent Chromium Compounds

The water soluble hexavalent compounds are extremely irritating, corrosive, and toxic to human body tissue; they penetrate surface tissue before they react. Insoluble chromium compounds, on the other hand, are retained in the lungs over extended periods of time and play a role in the production of lung cancer.[8] Chromium in the hexavalent form is clearly a cause of ulceration and perforation of the nasal septum.[8] The septum is particularly susceptible to the action of chromium not only because of the immediate contact of inhaled particles with the septum, but also because of its structure; i.e., the mucous membrane covering this area is far less vascular than the mucous membrane lining the rest of the nasal fossae and thus is easily destroyed. Other sites where ulcers may appear as a result of contact with chromium^{+6} are the skin, the roots of the fingernails, the knuckles, the eyelids, the edges of the nostrils, the toes and rarely the throat.[8]

General

The chromium metal itself is stable and relatively nontoxic because of its insolubility in water and body fluids.[8] Chromium, a trace element essential for sugar and fat metabolism, is necessary for the action of insulin.[8] Chromium deficiency in the diet of animals causes a syndrome simulating diabetes. A lack of chromium has also been associated with atherosclerotic heart disease, elevated cholesterol levels in the blood, and high fat content of the aorta. In areas where atherosclerosis is mild or absent, more chromium is found in body tissue than where the disease is endemic.[8]

The toxic dose of chromium for man is reported to be about 0.5 g $K_2Cr_2O_7$.[5] The toxicity of chromium salts toward aquatic life varies with the species, temperature, pH, valence, of the chromium, and synergistic or antagonistic effects, especially that of hardness.[5] Fish are relatively tolerant of chromium salts, but lower forms of aquatic life are extremely sensitive. There appears to be no evidence to lead to a conclusion that hexavalent chromium is more toxic toward fish than the trivalent form. Toward fish and other aquatic organisms the toxicities of trivalent and hexavalent chromium compounds have been reported as given in Table 2: Table 3 summarizes the reported effects of hexavalent chromium toward mammals.

Table 2. Toxicities of Chromium Compounds to Selected Aquatic Organisms[5]

Concentration of Chromium mg/l	Compound Used	Type of Organisms	Remarks
52	$K_2Cr_2O_7$	Young eels	Tolerated for 50 hours
5.2	$K_2Cr_2O_7$	Brown trout	Toxic
20	$K_2Cr_2O_7$	Rainbow trout	Toxic at 18°C
1.2	$Cr_2(SO_4)_3$	Sticklebacks	Lethal limit
2.0	$Cr_2(SO_4)_3$	Sticklebacks	Survived only 2 days
5.2	$KCr(SO_4)_2$	Young eels	Survived an aver. of 18.7 hours
0.05	-----	Daphnia magna	Killed in 6 days
0.21	$K_2Cr_2O_7$	Protozoan (Microregma)	Threshold effect
1.4	Na_2CrO_4	Gammarus pulex	Total mortality
40.6	$K_2Cr_2O_7$	Snail	Hardwater TL_m, 20°C
0.7	$K_2Cr_2O_7$	E. coli	Threshold effect
148	CrO_4	Polycelis nigra	Toxic threshold

Table 3. Toxicological Responses of Mammals to Hexavalent Chromium[14]

Animal	Route	Material	Average Dose or Concentration	Duration	Effect
Rabbit & Cat	IH	Chromates	1-50 mg/m^3	14 hr/day for 1-8 months	Pathological changes to lungs
Rabbit	SC	$K_2Cr_2O_7$	20 mg	-----	Lethal
Rabbit	IV	$K_2Cr_2O_7$	0.7 cc of 2% solution per kg body wt.	-----	Fatal
Mouse	IH	Mixed dust containing	7 mg/m^3 as CrO_3	37 hours over 10 days	Fatal
Mouse	IV	Zinc chromate	0.75 mg	1 dose	Fatal
Mouse	IV	$K_2Cr_2O_7$	0.7 cc of 2% solution per kg body wt.	-----	Fatal
Dog	IV	$K_2Cr_2O_7$	210 mg as Cr	-----	Rapidly fatal
Dog	SC	$K_2Cr_2O_7$	210 mg as Cr	-----	Rapidly fatal

*IH - inhalation; IV - intravenous; SC - subcutaneous.

Chromium is present in trace amounts in soils and in plants, but there is no evidence that chromium is essential or beneficial for plant nutrition.[17] Generally, concentrations of trivalent or hexavalent chromium in excess of 1.0 mg/kg of soil inhibit nitrification. On the other hand, the addition of 5 mg of chromium per kg of soil resulted in a slight increase of the nitrogen content of peas. Chromium is picked up by plants from the soil, for vegetables grown on soil irrigated with waste waters containing chromium had 3-10 times more chromium than those grown in similar soil devoid of chromium containing irrigation water.[17]

C. Environmental Properties

The drinking water standard is 0.05 mg/liter for hexavalent chromium[5]; the recommended standard for trivalent chromium is likewise 0.05 mg/liter.[6] The chromium containing sludges when occurring as a result of the standard reduction/hydroxide precipitation treatment methods can present a twofold toxicological hazard if landfilled.[6] The sludges can contain soluble chromium salts and complexes which, if leached out of the fill, can be detrimental. It is also possible for acid species to be landfilled with the hydroxide sludges, dissolve them, forming water soluble chromium compounds. Those water soluble materials can find their way to a potable water table from an inadequately placed landfill site.[6]

One of the problems with heavy metals is their tendency to concentrate through both aquatic and terrestrial food chains.[22] Aquatic macro- and microflora and fauna accumulate heavy metals such as cadmium in body tissues in significantly greater concentrations than present in the surrounding environment. These organisms are the food source for fish and insects which retain the cadmium in the tissues of the consumed organisms. The fish and insects are consumed in turn by larger organisms; this process continues to the organisms at the top of the pyramidal food chain, such as man and large carnivorous birds and mammals. The more links in the chain, the more severe the bioaccumulation phenomenon.

D. Radioactive Properties: None

Cobalt and Its Compounds

A. Physical/Chemical Properties

Elemental Cobalt (Co)

Cobalt (a.w. 58.93, m.p. 1493°C, b.p. 3550°C, d. 8.92)[9] is a silver-grey, hard, magnetic, ductile, somewhat malleable metal which crystallizes in hexagonal or cubic form.[1] Cobalt is stable in air or toward water at ordinary temperature. It is readily soluble in dilute nitric acid but only very slowly attacked by hydrochloric acid or cold sulfuric acid. The hydrated salts of cobalt are red; the soluble salts form red solutions which become blue on adding concentrated hydrogen chloride.

Cobaltous Oxide (CoO)

The cubic green-brown crystals[9] of this salt readily absorb oxygen even at room-temperature.[1] It is practically insoluble in water but is soluble in acids or alkali hydroxides. Cobaltous oxide is easily reduced to cobalt by carbon or carbon monoxide. Cobaltous oxide reacts at high temperatures with silica, alumina, and zinc oxide to form pigments.[1] It is formed by the calcination of cobalt carbonate or its oxides at high temperatures in a neutral or slightly reducing atmosphere.[7]

Cobaltous-Cobaltic Oxide (Co_3O_4)

Cobaltous-cobaltic oxide (m.w. 240.82, transition point 900-950°C) is a grey-black crystalline powder which above 900°C loses oxygen to form CoO.[1] It absorbs oxygen at lower temperatures but the crystalline structure is unchanged. Co_3O_4 absorbs water but no definite hydrate has been identified. It is reduced to elemental cobalt by carbon, carbon monoxide or H_2. This cobalt oxide is soluble in concentrated acids and alkalis although practically insoluble in water.

Cobaltic Oxide (Co_2O_3)

This steel-grey or black powder (m.w. 165.88, d. 4.81-5.60, m.p. decomposes at 895°C)[4] is formed when cobalt compounds are heated at a low temperature in the presence of an excess of air or by oxidizing neutral cobalt solutions with $NaOCl$.[1] It is converted to Co_3O_4 above 265°C.[1] Although practically insoluble in water, it is slowly soluble in hot HCl or hot dilute H_2SO_4 with the evolution of Cl_2 or O_2.[1]

Cobaltous Chloride ($CoCl_2$)

Cobaltous chloride (m.p. 724°C in HCl gas, d. 3.348, b.p. 1049°C, m.w. 129.84) is composed of pale-blue hygroscopic leaflets which appear colorless in very thin layers; this cobaltic salt turns pink on exposure to moist air.[1] Cobaltous chloride decomposes on long heating in air at 400°C; it sublimes at 500°C in HCl gas, forming iridescent, fluffy, colorless crystals. It is soluble in water, alcohols, acetone, ether and glycerol. $CoCl_2$ also occurs in a hydrated form.

Anhydrous cobaltous chloride becomes saturated in 96°C water at a concentration of 1050 g/liter whereas at 7°C its solubility is 450 g/liter.[6] In alcohol it is soluble to the extent of 544.0 g/liter and in acetone 86.0 g/liter.[6]

Cobaltous Chloride Hexahydrate ($CoCl_2 \bullet 6H_2O$)

This hydrated form of cobaltous chloride exists as a pink to red, slightly deliquescent, monoclinic, prismatic, crystalline material.[1] On heating, $CoCl_2.6H_2O$ (m.w. 237.93, m.p. 86.75°C, b.p.-$6H_2O$ at 110°C)[9] loses four water molecules at 52-56°C forming the dihydrate, violet or blue crystals which are stable unless exposed directly to moisture. It loses another water molecule at 100°C giving a monohydrate, violet, hygroscopic, amorphous solid or needles. The remaining water molecule is lost at 120-140°C. Hexahydrated cobaltous chloride is soluble in alcohols, acetone, ether and glycerol. Its solubility in water at 0°C is 767.0 g/liter and in water at 100°C it solubilizes to the extent of 1907.0 g/liter.[9]

Cobaltous material is an oxidizing material which, in contact with organic or other readily oxidizable substances may cause a violent reaction or combustion.[6] Cobalt salts hydrolyze to produce acid solutions. The pH of a 0.2 M aqueous solution of cobaltous chloride hyxahydrate is 4.6.[1]

Solutions containing cobaltous ions (Co^{++}) are relatively stable but cobaltic ions (Co^{+++}) are powerful oxidizing agents and consequently they are unstable in natural waters.[5]

B. Biological Properties

Elemental Cobalt

In humans, the level of cobalt toxicity is low, about equivalent to a daily dietary intake of 150 ppm.[8] Cobalt has been administered in the treatment of nephritis, in infections, and in anemias during pregnancy. However, its use has led to serious toxic manifestations, including thyroid enlargement, myxedema (a disease caused by thyroid deficiency) and congestive heart failure in infants. In mice, rabbits, and domestic animals, excessive doses of cobalt have caused polycythemia which overtaxes the heart and is associated with high blood pressure.[8]

Little is known about the effect of cobalt as a constituent of ambient air.[8] In hard metal manufacturing it has been a source of pulmonary fibrosis. Powdered cobalt is used as a bonding material in the manufacture of cutting tools that contain tungsten and carbide. In such factories fine particulate dust measuring less than 2.0 microns in diameter is generated and spreads into areas where it is not in use. Whereas powdered tungsten carbide has little or no irritant effect on the lungs, powdered cobalt produces chronic lung changes leading to pulmonary fibrosis, with chronic cough and shortness of breath. This disease is usually fatal if not diagnosed early.

When ingested with food, cobalt affects the heart and the thyroid gland.[8] In 1965 and 1966 an epidemic of a serious heart disease occurred in Quebec, Canada. Of 48 persons so afflicted, twenty died in shock. The essential symptoms were shortness of breath, pain in the heart and stomach area, cough, swelling of ankles, and general weakness. After numerous agents had been ruled out as the possible cause, it became apparent that the only individuals who had contracted the disease were those who had imbibed large amounts of beer. Changes in the thyroid gland of the diseased persons showed features characteristic of cobalt intoxication. The disease was promptly eliminated upon discontinuance of the use of cobalt in processing beer. Although the doses of ingested cobalt compounds in these cases were much greater than those of atmospheric contamination these findings are of interest in view of the lack of data concerned with long term cobalt ingestion and inhalation in minute concentrations.

Cobaltous Compounds (Co^{++})

Trace amounts of cobaltous ion appear to stimulate the growth of some organisms.[5] A definite growth response in the protozoan ciliate, Tetrahymena sp., was produced by 0.0005 mg/liter of cobalt, while the optimum total growth and rate of growth occurred at 0.008 mg/liter. The addition of 1-5 mg/liter of cobalt, as cobalt chloride or cobalt sulfate, to a medium used in the propagation of actinomycetes gave conspicuous growth.

At higher concentrations, however, cobalt ions have demonstrated pronounced toxic effects. The lethal concentration for the stickleback, Gasterosteus oculeatus, was 10 mg/liter of cobalt ion.[5]

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Below summarizes the toxicity of cobalt and two of its compounds towards certain mammals.

Toxicological Responses of Selected Mammals to Cobalt[7]

Co:	ORI-rat	LDLo:	1500 mg/kg
	ims-rat	TDLo:	112 mg/kg
$CoCl_2$:	ORI-rat	LD50:	180 mg/kg
	ORI-mouse	LD50:	80 mg/kg
	SCU-mouse	LDLo:	100 mg/kg
	ORI-guinea pig	LD50:	55 mg/kg
CoO:	ims-rat	TDLo:	90 mg/kg

C. Environmental Properties

The water quality standard for cobalt and its compounds is 0.05 mg/liter as Co.[6]

D. Radioactive Properties: None

Copper and Its Oxides

A. Physical/Chemical Properties

Copper (Cu)

Elemental copper (a.w. 63.54, m.p. 1083°C, b.p. 2595°C, d. 8.94)[9] dissolves readily in nitric and hot concentrated sulfuric acid; it solubilizes slowly in hydrochloric and dilute sulfuric acid but only when exposed to the atmosphere.[1] Copper is more resistant to atmospheric corrosion than iron, forming a green layer of hydrated basic carbonate.[4] It is noncombustible except as powder.[4] Metallic copper is insoluble in water.[4]

Cuprous Oxide (Cu_2O)

Copper (I) oxide (m.w. 143.08, m.p. 1232°C, b.p. 1800°C, d^{25}_{4} 6.0)[9] exists as octahedral crystals[4] or microcrystalline powder, the color varying from yellow, red or brown, depending on the method of preparation and the particle size.[1] This oxide is stable in dry air but gradually oxidizes to CuO in moist air.[1] It is insoluble in water and alcohol but soluble in hydrochloric acid, ammonium chloride, ammonium hydroxide and slightly soluble in nitric acid.[1]

Cupric Oxide (CuO)

Copper (II) oxide (m.w. 79.54, m.p. 1326°C, d. 6.3-6.49)[9] occurs as a black to brownish-black amorphous or crystalline powder or granules.[1] It is soluble in dilute acids, alkali cyanides and $(NH_4)_2CO_3$ solutions; it is slowly soluble in ammonia.[1] Cupric oxide is slightly soluble in water; at a pH 9 it solubilizes to a concentration of 1.54×10^{-5} mg/liter as Cu^{++} in pure water.[18] As the pH decreases, the solubility of cupric oxide increases such that at pH 5 its saturation concentration is 313.0 mg/liter as Cu^{++}.[18]

B. Biological Properties

Copper is found in traces in all plant and animal life; it is believed to be essential for nutrition.[5] The physiological function of copper appears to be involved in the metabolism of iron, for the utilization of iron by the blood-forming organs does not occur properly in the absence of copper. The copper requirement is reported to be about 2 mg/day for children and 3 mg/day for adults.[5]

In general, the soluble ionized salts of copper are much more toxic than the insoluble or slightly dissociated compounds.[2] Probably the most poisonous salts are the chloride and the subacetate.[2] Cuprous chloride is said to be twice as toxic as the more common cupric salt, but no major toxicological distinctions are recognized between the two valence states of copper.[2] As the sublimed oxide, copper may be responsible for one form of metal fume fever.[3] Inhalation of copper dust has caused, in animals, hemolysis of the red blood cells, deposition of hemofusion in the liver and pancreas, and injury to the lung cell; injection of the dust has caused cirrhosis of the liver and pancreas, and a condition closely resembling hemochematosis, or bronzed diabetes.[3] However, considerable trial exposure to copper compounds has not resulted in such disease.[3]

As regards local effect, copper chloride and sulfate have been reported as causing irritation of the skin and conjunctivae which may be on an allergic basis.[3] Cuprous oxide is irritating to the eye and upper respiratory tract. Discoloration of the skin is often seen in persons handling copper, but this does not indicate any actual injury from copper.[3]

Copper resembles many other heavy metals in its systemic toxic effects: widespread capillary damage, kidney and liver injury, and central nervous excitation followed by depression.[2] Hemolytic anemias are described in acute poisoning in man and chronic poisonings in sheep. Copper appears to be less deleterious than most heavy metals when ingested continuously in small amounts, but chronic feeding to animals results in a pigmentary cirrhosis of the liver.[2]

Acute poisoning from the ingestion of copper salts is rarely severe, if the metal is removed promptly by enesis.[2] Vomiting is provoked chiefly by the local irritant and astringent action of ionic copper on the stomach and intestines.[2] If vomiting fails to occur, gradual absorption from the bowel may cause systemic copper poisoning. Death is delayed for several days and apparent recovery may be followed by a fatal relapse.[2]

A type of chronic copper poisoning in man is recognized in the form of a metabolic disease called hereditary hepatolenticular degeneration (Wilson's disease).[2] Tissue copper levels are elevated in Wilson's disease, and this accumulation has been noted to precede the development of liver pathology, which may ultimately prove fatal.[2] If dietary copper intake is reduced and urinary excretion promoted, the neurologic signs and symptoms associated with Wilson's disease are alleviated. BAL, calcium disodium edetate and sulfur-containing amino acids can mobilize tissue copper stores for excretion; at least BAL has been shown to produce some clinical improvement, but repeated injections frequently give rise to undesirable side effects.[2]

Because copper in concentrations high enough to be dangerous to human beings renders water disagreeable to taste, it is believed by some that copper is probably not a hazard in domestic water supplies; although in excessive quantities it has been found toxic to a wide variety of aquatic forms, from bacteria to fish.[5] The toxicity of copper to aquatic organisms varies significantly not only with the species, but also with the physical and chemical characteristics of the water such as its hardness, temperature, turbidity and carbon dioxide content.[5] In hard water, the toxicity of copper salts is reduced by the precipitation of copper carbon-

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ate or other insoluble compounds.[5] The toxicity of copper to fish varies greatly depending on the presence of magnesium salts and phosphates. In the control of Chironomus sp. larvae, copper and chlorine together act synergistically to increase the toxicity of each acting alone. The sulfates of copper and zinc and of copper and cadmium are synergistic in their toxic effect on fish. Synergism also exists between copper and mercury and between copper and pentachlorophenate. On the other hand, sodium nitrite and sodium nitrate have been reported to decrease the toxicity of copper sulfate to fish, and copper has shown evidence of decreasing the toxicity of cyanide.[5]

C. Environmental Properties

The water quality standard for copper and its oxides is 1.0 mg/liter as Cu.[5]

Many copper salts are highly soluble as cupric or cuprous ions.[5] Copper salts occur in natural surface waters only in trace amounts, up to about 0.05 mg/liter so that their presence is generally the result of pollution, attributable to the corrosive action of the water on copper and brass tubing, to industrial effluents, or frequently to the use of copper compounds for the control of undesirable plankton organisms.[5] The chloride, nitrate and sulfate of divalent copper are readily soluble in water, but the carbonate, hydroxide, oxide and sulfide are not.[5] Indeed, cupric ions introduced into natural waters at pH 7 or above will quickly precipitate as the hydroxide or as basic copper carbonate, $CuCO_3.Cu(OH)_2.H_2O$, to be removed by absorption and/or sedimentation. As a result, copper ions are not likely to be found in natural surface waters or ground water.[5]

Investigations of the chemical fate of copper salts in the soil, especially with respect to organic matter and carbonate content of the soil have been conducted.[5] It was found that when copper sulfate was added to irrigation water at a concentration of 20 mg/l, $CuSO_4$er, it reached an equilibrium in the soil at 1.0 mg/liter after 6 hours at 20°C. Copper retention in the soil appears to be correlated more with organic matter and soil alkalinity than with the clay content of the soil, and organic matter appears to be more effective than carbonates in retaining copper.[5]

One of the problems with heavy metals is their tendency to concentrate through both aquatic and terrestrial food chains.[22] Aquatic macro- and micro- flora and fauna accumulate heavy metals, such as copper, in body tissues in significantly greater concentrations than present in the surrounding environment. Important mechanisms for uptake of copper and other heavy metals include: absorption from the soil and sediments by plants, ingestion by stream bottom feeders and by detrius feeders. The aquatic macro- and micro- flora and fauna are the food source for fish and insects which retain the copper in the tissues of the consumed organisms. The fish and insects are consumed in turn by larger organisms; this process continues to the organisms at the top of the pyramidal food chain, such as man and large carnivorous birds and mammals. The more links in the chain, the more severe the bioaccumulation phenomenon.[22]

D. Radioactive Properties: None

Cyanides

A. Physical/Chemical Properties

Sodium Cyanide (NaCN)

Sodium cyanide (m.w. 49.02, m.p. 563°C, b.p. 149°C)[9] is a white, deliquescent, crystalline powder[3] which is odorless when perfectly dry; somewhat deliquescent in damp air and emits a slight odor of HCN.[1] It is freely soluble in water (480.0 g/liter at 10°C, 820.0 g/liter at 35°C) but only slightly so in alcohol.[9] The aqueous solution is strongly alkaline and rapidly decomposes[4]; the solution readily dissolves gold and silver in the presence of air.[1]

Hydrogen Cyanide (HCN)

Hydrogen cyanide (m.w. 27.03, d_{gas} 0.941, d_{liquid} 0.687, m.p. -14°C, flash point 0°F)[9] is a colorless gas or liquid with a characteristic odor of bitter almonds.[5] It is very weakly acid (does not redden litmus) and burns in air with a blue flame.[1] This cyanide boils at 26°C and is highly soluble as a gas or miscible with water and alcohol as a liquid; it is slightly soluble in ether.[5] In water, the ratio of cyanide ion to undissociated HCN is a function of pH.[5] At pH values of

7 or below, less than 1 percent of the cyanide molecules are in the form of cyanide ion: at pH 8 only 6.7 percent, at pH 9 only 42 percent and at pH 10, 87 percent of cyanide is dissociated.[5]

When not absolutely pure or stabilized, HCN polymerizes spontaneously with explosive violence.[4] Hydrogen cyanide is a severe explosion hazard when exposed to heat or flame by chemical reaction with oxidizers.[3] In contact with alkaline materials, hydrogen cyanides can polymerize or decompose explosively. The liquid is commonly stabilized by the addtion of acids.[3] The solubility of HCN in water at -0.9°C is 0.81 mol%, at -35°C is 3.09 mol% and at -15.50°C it solubilizes to 26.29 mol%.

Ferric Ferrocyanide ($Fe_4(Fe(CN)_6)_3$)

Ferric ferrocyanide (m.w. 859.3)[9] exists as a dark blue powder[1] or crystals[3] which are insoluble in dilute acids, organic solvents, water, alcohol and ether but soluble in concentrated HCl and H_2SO_4. It is unstable to alkalis of all concentrations or reducing media. When freshly prepared ferric ferrocyanide is soluble in aqueous oxalic acid. Acid, basic or neutral solutions of ferrocyanides liberate hydrocyanic acid upon irradiation.[3]

B. Biological Properties

HCN and Cyanide Salts

Hydrogen cyanide and the cyanides are true protoplasmic poisons.[3] Cyanide is a potent and rapidly acting chemical asphyxiant; it deprives tissues of necessary oxygen by inhibiting reversibly such oxidative enzymes as cytochrome oxidase.[2] Because of the inability of the tissues to remove the oxygen from the blood, venous blood retains the bright/red color of oxyhemoglobin. Cyanide does not react to an appreciable extent with the hemoglobin molecule. As with other chemical asphyxiants, the critical organs are those which are most sensitive to oxygen lack, notably the brain. A transient stage of central nervous stimulation is followed by central nervous depression and finally hypoxic convulsions and death due to respiratory arrest. Cardiac irregularities are commonly observed, but the heart beat invariably outlasts breathing movements.[2]

Few poisons are more rapidly lethal than cyanide. The inhalation of hydrogen cyanide commonly produces reactions within a few seconds and death within minutes.[2] HCN in aqueous solution (hydrocyanic acid) is readily absorbed from the skin and from all mucous membranes, but the alkali salts are usually toxic only when ingested. The average lethal dose of HCN taken orally is believed to lie between 60 and 90 mg (1 to 1.5 grains), this corresponds to about 1 teaspoonful of a 2 percent solution of HCN and to about 200 mg potassium cyanide. The lethality of most derivatives is regarded as proportional to the content of readily available cyanide. The mortality rate is high, but in nonfatal cases recovery is generally complete. Rarely neuropsychiatric sequelae are observed, as in carbon monoxide poisoning.[2]

Cyanide in reasonable doses (10 mg or less) is readily converted to thiocyanate in the human body and in this form is much less toxic to man.[14] Usually, lethal toxic effects occur only when the detoxifying mechanism is overwhelmed.[14] In the detoxification mechanism the cyanide is converted to the thicyanate ion by an enzymatic reaction which is mediated by the enzyme rhodanese.[2] This enzyme is widely distributed in tissues, but the greatest activity is found in the liver.[2] The body has a large capacity to detoxify cyanide, but the rhodanese system responds sluggishly to a cyanide challenge. Also, a reverse reaction mediated by thiocyanate oxidase occurs in mammalian erythrocytes. Thus, a major factor in the time to the appearance of toxic signs or death is the rate at which cyanide is absorbed.[2]

It is generally recognized that undissociated HCN is more toxic toward aquatic life than cyanide ion. The effective toxicant to fish in nearly all solutions of complex metallocyanides tested is molecular HCN, the complex ions are relatively harmless.[14] The total cyanide content of such solutions is not a reliable index of their toxicity since HCN derives from dissociation of the complex ions, which can be greatly influenced by pH changes. A more than thousand fold increase of the toxicity of the nickelocyanide complex is associated with a decrease of pH from 8.0-6.5. A change in pH from 7.8-7.5 increases the toxicity more than tenfold.[14]

Numerous investigators have shown that the toxicity of free cyanide increased at reduced oxygen concentrations. The toxic action is known to be accelerated markedly by increased temperature, but the influence of temperature during long exposure has not been demonstrated.[15] The toxicity of cyanide to diatoms varies little with change of temperature and was a little greater in soft water than in hard water.[14] For Nitzchia linearis, concentrations found to cause a 50 percent reduction in growth of the population in soft water (44 mg/liter Ca-Mg as $CaCO_3$) were 0.92 mg/liter CN at 72°F, 0.30 mg/liter at 82°F, and 0.28 mg/liter at 86°F. Cyanide appears to be more toxic to animals than to algae.[14]

Ferric Ferrocyanide

Ferrocyanides as such are of a low order of toxicity, although highly toxic decomposition products can form upon mixing them with hot concentrated acids.[3] Acid, basic or neutral solutions of ferrocyanides liberate hydrocyanic acid upon strong irradiation.[3] Potassium ferrocyanide in which the iron is in the reduced condition is readily soluble in water but the complex ions decompose slowly to release cyanide ion.[5] Sodium ferrocyanide in aqueous solutions decomposes under the action of sunlight to release cyanide ion and HCN. It has been shown that solutions containing the ferro and ferricyanide complexes become highly toxic to fish through photodecomposition upon exposure to light.[14]

C. Environmental Properties

The water quality standard for the cyanides (HCN or NaCN) is 0.01 mg/liter as CN.[6] Ferrocyanides and ferricyanides are less toxic than HCN or NaOH, but can release cyanide ion which forms HCN in the presence of heat and sunlight.[14] The relationship between potassium ferrocyanide and concentration resulting CN^- concentrations in bright sunlight are as follows:

The Release of CN^- by Photodecomposition of Potassium Ferrocyanide[14]

Concentration of $K_3Fe(CN)_6$ in (mg/l)	Resulting Concentration of CN^- in mg/liter
1	0.05-0.16
2	0.36-0.48
3	0.72
5	0.50-0.84

No water quality standard is available for ferrocyanides; however, the concentration of ferrocyanides should be such that no more than 0.01 mg/liter of cyanide ion would be released to the water under optimal conditions for ferrocyanide decomposition. Therefore 0.2 mg/liter is the recommended limiting concentration in water and soil.[14]

D. Radioactive Properties: None

Fluorine and Its Compounds

A. Physical/Chemical Properties

Fluorine (F_2)

Fluorine (a.w. 18.9984, b.p. −188°C, m.p. −217.8°C, d$_{gas}$$^{1\ 95}$, d.-200°C$^{1\ 14}$, flash point -219.6°C)[9] is a highly toxic and corrosive pale yellow gas with a sharp, penetrating and characteristic odor.[6] Fluorine is the most powerful oxidizing agent known, reacting with practically all organic and inorganic substances with the exception of the inert gases, metal fluorides in their highest valence state and a few pure completely fluorinated organic compounds.[6] Fluorine decomposes water giving hydrofluoric acid (HF), oxygen fluoride (OF_2), hydrogen peroxide, oxygen and ozone. It reacts, with nitric acid, forming the explosive gas fluorine nitrate (NO_3F) and with sulfuric acid, giving fluorosulfonic acid ($HFSO_3$). Fluorine yields the metal fluorides, water, oxygen and oxygen fluoride when made to react with metal hydroxides in the cold. It reacts violently with organic compounds, usually with disintegration of the molecule.

Sodium Fluoride (NaF)

Sodium fluoride (m.w. 42.00, m.p. 993°C, b.p. 4°C, d. 2.558)[9] exists as either clear, lustrous, cubic/tetragonal crystals or a white powder.[3] Its solubility in water at 15°C is 40.0 g/liter and at 25°C it is 43.0 g/liter while at 100°C NaF solubilizes to a concentration of 50.0 g/liter; it is very slightly soluble in alcohol.[9] Aqueous solutions of sodium fluoride have an alkaline reaction caused by partial hydrolysis.[1] The pH of a freshly prepared saturated solution of NaF is 7.4.[1] Aqueous solutions etch glass, but the dry crystals or powder can be stored in glass bottles.[1]

Calcium Fluoride (CaF_2)

Calcium fluoride (m.w. 78.08, d. 3.18, b.p. c.a. 2500°C)[4] occurs as either a white powder or cubic, colorless crystals which luminesce upon heating.[1] Calcium fluoride is only slightly soluble (15 mg/liter) at neutral pH's but as the pH of the solution decreases its solubility increases. See Figure 1.[25]

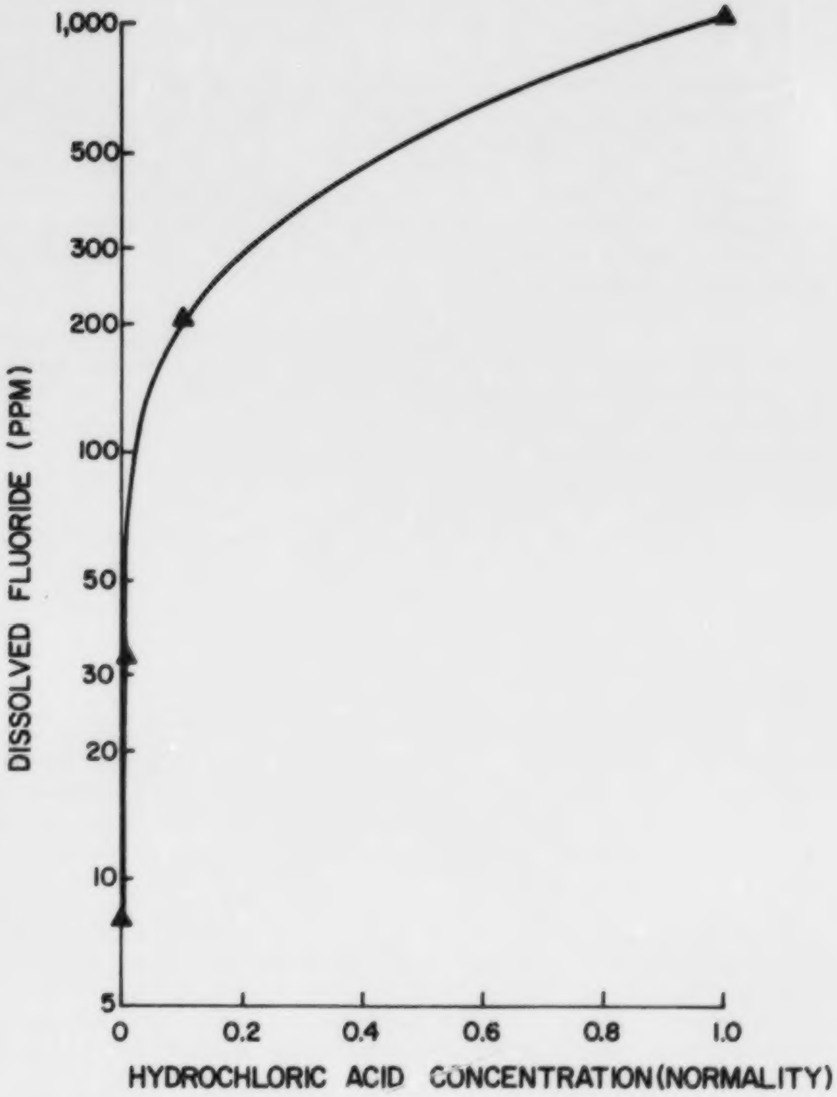
Hydrogen Fluoride (HF)

Hydrogen fluoride (m.w. 20.01, m.p. -83.1°C, b.p. 19.54°C, d_{liquid} 0.988)[9] is a colorless, fuming, mobile liquid or colorless gas[4] which is infinitely soluble in water, dissociating to hydrogen and fluoride ions.[1] It is also soluble in alcohol, slightly soluble in ether and soluble in many organic compounds, e.g. benzene, toluene, m-xylene, tetralin. Many compounds are soluble in HF.[1] White anhydrous HF is one of the most acidic substances known but in aqueous solution it is a weak acid ($K=7.4 \times 10^{-4}$).[1] Hydrogen fluoride dissolves silica, silicic acid and glass.[1]

B. Biological Properties

Fluorine/Fluoride

Fluoride is a "general protoplasmic poison," but it is not possible yet to describe in detail the mechanism by which it produces death.[2] At least four major functional derangements are recognized. Inhibition of one or more of the enzymes controlling cellular glycolysis may result in a critical lesion. Inhibition of cholinesterase activity noted in vitro, however, probably plays no role in fluorine poisoning even though pretreatment of rats with fluoride increases their sensitivity to succinylcholine, demiton and parathion. Shock due to fluid and electrolyte loss, central vasomotor depression and perhaps direct depression of vascular smooth muscle is an important contributory cause of death. Mild renal pathology (acute congestion and cloudy swelling of tubular cells) has been described in human fatalities but death in acute renal failure appears to be unknown both in man and animals. Chronic administration does not result in significantly more renal injury. Finally, the binding or precipitation of calcium as CaF_2 has been suggested as the mechanism



APPENDIX FIGURE I
SOLUBILITY OF CALCIUM FLUORIDE
IN HYDROCHLORIC ACID SOLUTIONS

underlying many diverse signs and symptoms in fluoride poisoning, particularly if death is delayed. It is not certain as to whether or not calcium binding plays a role in manifestations of central nervous system poisoning such as depression and occasionally epileptiform convulsions and respiratory failure.[2]

Besides being an inhibitor of glycolysis by virtue of its inhibition of the enzyme enolase, fluorine through its inhibition of other enzymes inhibits energy metabolism via the tricarboxylic acid cycle both by blocking the entry of pyruvate and fatty acids and by inhibiting succinic dehydrogenase.[8] Therefore, fluoride is not simply a glycolysis inhibitor but rather a general inhibitor of oxidative metabolism.

Chronic endemic fluorosis due to high concentrations of natural fluoride in local water supplies is characterized by mottling of the teeth, osteosclerotic changes in the skeleton and sometimes central nervous system involvement.[2] Fluorosis illustrates important toxicological properties of fluoride but not ones that are relevant to acute fluoride poisoning. Fluoride poisoning can be induced by any soluble compound which dissociates fluoride ion.[2] Hydrogen fluoride is less toxic than fluorine; the TLV is 3 ppm, 30 times that of fluorine.[6]

Hydrogen Fluoride

The ingestion of an estimated 1.5 grams of hydrogen fluoride produced sudden death without gross pathologic damage.[2] On the other hand, the repeated ingestion of small amounts of HF has resulted in moderately advanced fluoride osteosclerosis in man. Thus, hydrogen fluoride is capable of inducing the systemic manifestations of both acute and chronic fluoride poisoning. It possesses an additional hazard, however, because of its corrosive properties.[2] Respiratory exposure to high concentrations of HF fumes characteristically results in hemorrhagic pulmonary edema in man and animals. The potential hazard of this local reaction is equivalent to that of HCl or SO_2. Even though pulmonary involvement may dominate the clinical picture and the pathologic findings, systemic fluoride poisoning may still be the cause of death.[2]

Hydrogen fluoride, per se, is reported to be harmful to fish at 40 mg/liter and lethal at 60 mg/liter. It appears that the concentrations of fluoride will not interfere with the specified beneficial uses given:

Water Quality Criteria for Specific
Beneficial Uses of Water-Fluorides[5]

Domestic water supply	0.7-1.2 mg/liter
Industrial water supply	1.0 mg/liter
Irrigation water supply	10.0 mg/liter
Stock watering	1.0 mg/liter
Aquatic life	1.5 mg/liter

Sodium Fluoride

Clinical data indicates that the sodium salt of fluorine lies near the borderline between toxicity classes of "very toxic" (LD*human* 50-500 mg/kg) and "extremely toxic" (LD*human* 5-50 mg/kg).[2]

Calcium Fluoride

Calcium fluoride is considered moderately toxic with the lethal dose for humans ranging from 500-5000 mg/kg of body weight.[2] While oral ingestion of solid calcium fluoride would immediately release toxic quantities of fluoride, it would take a daily consumption of 3-10 liters of saturated calcium fluoride solution over a period of many years to produce fluorosis.

Although calcium fluoride does not deserve designation as a "severely hazardous" material as do leads, cadmiums etc., it is a potentially hazardous substance whose disposal obviates regulation. Calcium fluoride should be termed "moderately hazardous" whose Level III disposal technology would necessitate a disposal site isolated from natural ground water, and with surface coverings of clay, graded so as to virtually eliminate the entry of water into the waste.

Evidence offered by industry counter to the position that calcium fluoride is a potentially hazardous waste is exerpted below. The judgment of the authors is that, while factual, they do not establish the non-hazardous nature for this material:

(1) U.S. Dept. of Health, Education and Welfare Toxic Substances List (1973 Edition)

There are an estimated 15,000 separate substances included in this list of 25,043 items which includes cross-referencing. Calcium Fluoride is not included in this comprehensive listing of toxic substances.

(2) California State Water Resources Control Board - "Water Quality Criteria" (January 1973 Reprint)

Under the heading "Calcium Fluoride" on page 153 this document cites a report stating "the oral LD50 for guinea pigs is more than 5.0 grams/kg of body weight" and "the lethal dose required to kill the fish tinca vulgaris, is reported ---- to be 30,000 mg/l, which is far greater than the solubility."

These toxicological levels for Calcium Fluoride are quite similar to those reported for various domestic animals and numerous types of aquatic life in the section on sodium chloride (pages 264 and 265) of the California "Water Quality Criteria" Reference.

(3) In testimony submitted to the Illinois Pollution Control Board during hearings held in 1973 and 1974 on a petition to increase that state's effluent and water quality limitations for fluoride (IPCB No. R73-15), Dr. William F. Sigler (Dept. of Wildlife Science, Utah University) stated "in the presence of calcium, magnesium or a number of other things, it (fluoride) becomes substantially less toxic (R135)." Dr. Leonard A. Knauss appeared before The Board representing Olin Corporation as their Manager of Environmental Hygiene and Toxicology. Dr. Knauss testified, "If the fluoride is taken into the body in the form of a calcium fluoride solution, very little, if any, of the fluoride will be deposited in the bony tissue mainly because the bony tissue is composed of a calcium based material and, therefore, it probably would be excreted almost exclusively as calcium fluoride." (R 322).

Other testimony at the Illinois hearings noted that sodium fluoride is far more soluble than calcium fluoride and therefore fluoride toxicity studies on aquatic life are almost invariably done using sodium fluoride, because calcium fluoride simply will not dissolve at concentrations high enough to have any detectable effect on the species exposed.

C. Environmental Properties

Owing to their origin in only certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters.[5] In general, water containing less than 0.9-1.0 mg/liter of fluoride will seldom cause moltled enamel in children, and for adults concentrations less than 3-4 mg/liter are not likely to cause endemic cumulative fluorosis and skeletal effects.[5]

Fluoride added to soil or water has little or no effect on the fluoride content of plants grown in such soil.[5] The effects of fluorides in drinking water for animals in analogous to those for humans. Fluoride ions appear to have direct toxic properties toward aquatic life, and in addition there seems to be a relationship between the fluorides in water and the condition of the teeth of the fish.

The recommended provisional limits for fluorine in the atmosphere, in potable water and in marine habitats are as follows[6]:

Contaminant in Air	Provisional Limit
Fluorine	0.001 ppm
Contaminant in Water	
Hydrogen fluoride (as F_2/H_2O reaction product)	0.10 ppm

D. Radioactive Properties: None

Lead and Its Compounds

A. Physical/Chemical Properties

Elemental Lead (Pb)

Elemental lead (a.w. 207.19, d. 11.34, m.p. 327.4°C, b.p. 1744°C)[20] is a bluish-white, silvery, gray metal.[1] It is highly lustrous when freshly cut but tarnishes upon exposure to air.[1] Because of lead's softness and malleability it can be easily melted, cast, rolled and extruded.[1] Lead is soluble in hot concentrated nitric acid, in boiling concentrated hydrochloric or sulfuric acid, and in acetic acid. Lead is attacked by pure H_2O and weak organic acids in the presence of oxygen but is resistant to tap H_2O, hydrofluoric acid, brine and solvents.[1]

Lead Carbonate ($PbCO_3$)

Lead carbonate (m.w. 267.20, d. 6.6, m.p.(dec) 315°C)[9] exists as white, powdery crystals which are soluble in acids and alkalis, e.g. acetic acid or dilute nitric acid with effervescence.[1] Neutral lead carbonate is insoluble in ammonia, alcohols and practically insoluble in water (solubility at 20°C 0.0017 g/l).[9] Neutral lead carbonate is usually accompanied by the impurity basic lead carbonate.

Basic Lead Carbonate ($2PbCO_3 \cdot Pb(OH)_2$)

This lead carbonate (m.w. 775.60, d. 6.86, m.p.(dec) 400°C)[9] is a white amorphous powder which is soluble in acids (especially nitric acid), slightly soluble in aqueous CO_2 and insoluble in alcohols.[4] Basic lead carbonate solubilizes to the extent of 1.1-1.7 mg of $PbCO_3$/l at 20°C.[9]

Lead Sulfide (PbS)

Lead sulfide (m.w. 239.28, d. 7.13-7.7, m.p. 1114°C,b.p.(subl) 1281°C)[9] occurs as the mineral galena which exists as either silvery metallic crystals or a black powder[1] that is sparingly soluble in water (0.86 mg/l at 18°C/102.8 mg/l at 25°C), alcohols and alkalies but soluble in acids such as HNO_3 and hot dilute HCl.

Lead Sulfate ($PbSO_4$)

Lead sulfate (m.w. 303.28, d. 6.12-6.39, m.p. 1170°C)[9] is a white rhombic crystal with water solubilities of 42.5 mg/l (25°C), 28 mg/l (0°C) and 56 mg/l (40°C).[9] It is slightly soluble in concentrated H_2SO_4 but is insoluble in most acids. Lead sulfate is soluble in ammonium salts.[9]

Lead Chromate ($PbCrO_4$)

The yellow or orange crystals of lead chromate are (m.w. 323.22, d. 6.123, m.p. 844°C) soluble in acids (e.g. dilute HNO_3) and solutions of fixed alkali hydroxides but insoluble in acetic acid and ammonia.[4] Lead chromate is one of the more insoluble lead salts - one liter of water dissolving 0.2 mg.[1]

Lead Monoxide (PbO)

This compound (m.w. 223.21, d. 9.53, m.p. 888°C, b.p. 1472°C)[24] consists of a yellow to yellowish-red, heavy, odorless powder or minute tetragonal crystalline scales.[1] At 300-450°C in the air it is converted into Pb_3O_4 but at higher temperatures it reverts back to PbO.[1] Lead monoxide is insoluble in alcohol but is soluble in acetic acid, dilute HNO_3, ammonium chloride, strontium chloride and in warm solutions of fixed alkali hydroxides.[1] Its solubility in water is 17.0 mg/l.[9]

Lead Tetroxide (Pb_3O_4)

Pb_3O_4 (m.w. 685.63, d. 9.1, b.p.(dec.) 500°C)[9] is a bright-red, heavy powder which is insoluble in water and alcohol.[1] It is soluble in: hot HCl with the evolution of Cl_2; acetic acids; excess glacial acetic acid; dilute nitric acid in the presence of H_2O_2.[1] Lead tetroxide is an oxidizing agent and therefore will react with certain reducing agents.[4]

Lead Dioxide (PbO_2)

Lead dioxide (m.w. 239.21, d. 9.375, m.p.(dec) 290°C)[9] consists of dark brown hexagonal crystals[3] which evolve oxygen when heated, first forming Pb_3O_4 and at high temperatures PbO.[1] This lead oxide is soluble in glacial acetic acid,[4] in dilute HCl with the evolution of Cl_2,[1] in dilute nitric acid in the presence of H_2O_2,[1] in alkali iodine solutions with the liberation of iodine and in oxalic acid or other reducers.[1] Lead dioxide is insoluble in water and alcohol. It is an oxidizing agent and hence, reacts with reducing material; it is a dangerous fire risk in contact with organic materials.[4]

Lead Hydroxide ($Pb(OH)_2$)

Lead hydroxide (m.w. 241.20, d. 7.592, m.p. (dec) 145°C)[9] exists as a white, bulky powder[4] which is soluble in alkalis, nitric or acetic acid and fixed alkali hydroxides.[1] Its solubility at pH 9 is 8.54 mg Pb^{++}/l and at pH 7 is 150.0 mg Pb^{++}/l, and as the pH decreases further lead hydroxide's solubility increases by more than an order of magnitude.[20] It absorbs CO_2 from the air and decomposes at 14.5°C.[4]

Lead Molybdate ($PbMoO_4$)

$PbMoO_4$ (m.w. 367.16, d. 692, m.p. 1060-1070°C)[9] is a yellow powder which decomposes in concentrated H_2SO_4.[3] It is soluble in acids and KOH and insoluble in water and alcohol. It is noncombustible.

B. Biological Properties

The toxicity of the various lead compounds appears to depend upon:[3]

a). the solubility of the compound in the body fluids;
b). the fineness of the particles of the compound, solubility being greater in proportion to the fineness of the particles;
c). conditions upon which the compound is being used; where a lead compound is used as a powder, contamination of the atmosphere will be much less where the powder is kept damp.

The solubility of some of the lead compounds in the blood serum at 25°C in mg/liter are:[21]

PbO	1152.0
Pb	578.0
$PbSO_4$	43.7
$PbCO_3$	33.3

Lead is poisonous in all forms. It is one of the most hazardous of the toxic metals because the poison is cumulative and toxic effects are many and severe.[2] Of the various lead compounds, the carbonate, monoxide and sulfate are considered to be more toxic than elemental lead or other lead compounds. The toxicity of lead chromate is less than would be expected, due to its low solubility. All of the lead compounds are sufficiently soluble in digestive juices to be considered toxic.[2]

In soft H_2O, lead may be very toxic whereas in hard H_2O equivalent concentrations of lead are less toxic. Calcium in a concentration of 50 mg/l has destroyed the toxic effect of 1.0 mg/l of lead.[5] Immunity to lead cannot be acquired and sensitivity to lead seems to increase with exposure.

Lead may enter the human system through inhalation, ingestion or skin contact.[6] Direct skin contact is of negligible importance in connection with inorganic lead compounds. However, in the case of organic lead compounds, skin contact can be a real hazard. Industrially, inhalation of dust, mist or fumes, is the chief method by which lead and its inorganic compounds may enter the body.[6]

Lead poisoning is rated as 10 times more liable to occur from breathing lead dust than from swallowing it.[21] This is probably due to the fact that the liver filters out swallowed substances like lead and removes them from the blood before harm can be done. If they are breathed, they are taken up by the blood stream, pumped all over the body and thus make themselves felt more readily than would otherwise be possible. Lead is thought to be toxic only when present in the systemic circulation. Thus it can be stored by the body and only becomes a danger when it is returned to circulation in greater amounts than the body can safely eliminate.[21]

Following ingestion of a large amount of any insoluble lead salt (especially the acetate, carbonate or chromate), the signs and symptoms are due largely to local irritation of the alimentary tract.[2] If absorption is sufficient, pain, leg cramps, muscle weakness, paresthesias, depression, coma, and death may follow within 1 or 2 days. Three clinical syndromes are recognized in the diagnosis of chronic plumbism:[2]

a). The alimentary type is characterized by anorexia, a metallic taste, constipation and severe abdominal cramps (lead colic due to intestinal spasm)[2];

b). The neuromuscular type is characteristic of adult plumbism which consists of peripheral neuritis limited to the extensor muscles. Weakness or paralysis may occasionally be accompanied by arthralgia and myalgia, but sensation is otherwise unaffected. As produced in laboratory animals a decrease in motor nerve conduction velocity is associated with segmental demyelination.[2]

c). The cerebral type of lead poisoning (lead encephalopathy) is the most common type in children. Encephalopathy is a complication in about 50% of lead poisoning cases and the mortality rate among patients developing cerebral involvement is about 25%.[2]

The daily intake of lead in food/beverages is approximately 0.3 mg which the human body is capable of eliminating daily. However, if more lead is ingested than excreted (0.3-1.0 mg/day)[5] a condition exists which is referred to as "chronic lead poisoning", which may develop within weeks or months.[6] Many acute poisonings, however, subside without sequelae, since the absorption of lead from the bowel is inherently slow and incomplete.[2] Presumably this outcome is also favoured by vigorous treatment. As long as the body, however, contains excessive amounts of lead fixed in the tissues, symptomatic recurrences are an ever present threat. In all recurrent episodes there is a characteristic rise in the lead concentration of the body fluids and excreta.[2] A lead content of blood greater than 0.005% and of urine greater than 0.08 mg/l support a diagnosis of lead poisoning.[2]

Lead accumulates in bones, where it replaces calcium.[8] Bones store almost one half of the total body pool, with long bones (arms and legs) accumulating about 3 times more than flat bones (breast bone, vertebrae). Becker and coworkers found 5ppm lead in ancient bones 500 years old in comparison to 50 ppm which is present in bones today. They implicated contemporary air pollution as the primary cause of this increase.[8] With advancing age, some of the metabolized lead accumulates in soft tissues. Newly absorbed lead is retained in the body as lead triphosphate, especially in liver, kidneys, pancreas, and aorta.[8]

Plants growing on soils containing 1 ppm of lead have shown 20-25 ppm lead per gram in their ash. Samples taken from different portions of a plant vary considerably in their lead content.[8]

It is thought that inorganic lead salts in irrigation water may be toxic to plants although toward giant kelp, Macrocystis pyrifera, lead was found to be less toxic than Hg, Cu, Cr^{+6}, Zn and Ni.[5] Lead nitrate produced no deleterious effects on the rate of photosynthesis of kelp in sea H_2O during a 4-day exposure at 4.1 mg Pb/liter.[5]

The toxicity of lead and some of its compounds towards certain rodents is shown below:

Toxicological Responses of Rodents to Lead and Lead Compounds

$PbCO_3$ (neutral)	ipr-LD_{ca}: 124 mg/kg, guinea pig[7]
(basic)	orl-MLD: 1.0 g/kg, guinea pig[1]
$PbSO_4$	ipr-LD_{50}: 300 mg/kg, guinea pig[7]
Pb (elemental)	ipr-LD_{Lo}: 100 mg/kg, guinea pig[7]
PbO	ipr-LD_{50}: 400 mg/kg, rat[7]
PbO_2	ipr-LD_{Lo}: 115 mg/kg, guinea pig[7]

C. Environmental Properties

The water quality standard for all lead compounds is 0.05 mg/l as lead.[6] The solubilities of all lead compounds discussed in this report fall above this concentration: $Pb(OH)_2$, 150 mg/l; PbO, 64 mg/l; $PbSO_4$, 42 mg/l; $PbCO_3 \cdot Pb(OH)_2$, 1.1-1.7 mg/l; $PbCO_3$, 1.7 mg/l; $PbCrO_4$, 0.1 mg/l, therefore surface disposal or landfilling procedures must provide for adequate protection of surface and ground waters. Disposal by landfill techniques in a California Class I type disposal site would be adequate providing a "California type" climate exists; in other areas protection would need to be more rigorous.

Under certain conditions lead is solubilized as either the chloride or the sulfate which are both slightly soluble and hence landfill disposal of lead is not recommended under certain conditions.[6] The characteristics of water, soft or hard, that appear to be conducive to plumbo-solvency, include comparative absence of calcium and magnesium bicarbonates, low pH, high dissolved oxygen, and high nitrate content.

One of the problems with heavy metals is their tendency to concentrate through both aquatic and terrestrial food chains.[22] Aquatic macro- and micro-flora and fauna accumulate heavy metals such as lead in body tissues in significantly greater concentrations than present in the surrounding environment. These organisms are the food source for fish and insects which retain the heavy metals in the tissues of the consumed organisms. The fish and insects are consumed in turn by larger organisms, this process continues to the organisms at the top of the pyramidal food chain, such as man and large carnivorous birds and mammals. The more links in the chain, the more severe the bioaccumulation phenomenon.

For lead and its compounds, this bioaccumulative phenomenon is less acute. Lead accumulates in the bones (and/or exoskeleton) of animals in somewhat greater proportions than in other tissues.[8] Since the bones and exoskeleton of most larger animals are not consumed, the lead contained therein is not available to top carnivores. Also lead compounds tend to interact with soil particles to form complexes which are not readily available to plant uptake. Although plants do accumulate lead from soil and because lead is translocated poorly, it tends to remain in the roots and return to the soil when the plant dies. Leaves readily accumulate air-borne lead compounds in the leaf tissue, and most of the lead will still be in the leaves when they are consumed by other organisms.

D. Radioactive Properties: None

Manganese Dioxide (MnO_2)

A. Physical/Chemical Properties

MnO_2 (m.w. 86.94, d. 5.026)[9] is a black, crystalline manganese salt[4] which is insoluble in water, nitric acid and sulfuric acid but is soluble in hydrochloric acid with the evolution of Cl_2.[1] In the presence of hydrogen peroxide or oxalic acid it dissolves in dilute H_2SO_4 or HNO_3.[1] Manganese dioxide is a strong oxidizer, hence it should not be heated or rubbed with organic matter or other oxidizable substances, such as sulfur, sulfides, phosphides, hypophosphites, etc.[1] Manganese dioxide decomposes to Mn_2O_3 and oxygen at 535°C.[1]

B. Biological Properties

Manganese is essential for the nutrition of both plants and animals, apparently as an enzyme activator.[5] It is especially abundant in the reproductive parts of plants, seeds being highest while woody sections contain the least manganese. Nuts contain the highest concentrations (22.7 mg/kg) and sea foods the lowest (0.25 mg/kg). Manganese has been used to enrich soil, yet in some concentrations it may be phytotoxic.[5]

Diets deficient in manganese result in impaired or abnormal growth, symptoms of central nervous system disturbance, anemia and possibly interference with reproductive functions.[8] These conditions have been associated with a low level of liver aldolase, an enzyme involved in carbohydrate metabolism, and of bone alkaline phosphatase activity, a condition that can be rectified by administering manganese. The metabolism of chlorine is linked with that of manganese; both decrease liver fat in rats and birds.[8] The daily intake for a normal human diet is about 10 mg. It is absorbed very slightly and deposits mainly in the liver and kidneys.

Typically, human toxicity to manganese and its salts is the result of chronic inhalation of the dust or fumes.[2] Manganese salts are poorly absorbed from the alimentary tract, hence acute systemic intoxication does not normally occur after ingestion. Systemic poisoning may occur from chronic ingestion or inhalation of manganese or one of its salts, although the consensus is that the only significant mode of entry is by inhalation of dusts or fumes.[2]

The clinical symptoms of manganese intoxication involve malfunctioning of the central nervous system, probably by enzyme inhibition.[6] Warning and diagnosis is complicated by an incubation period of 6-30 days prior to the onset of symptoms. A controlled, clinical study of Chilean miners suggests that a positive correlation exists between nutritional deficiency and susceptibility to manganism.[6]

In concentrations not causing unpleasant tastes, manganese is regarded by most investigators to be of no toxicological significance in drinking water.[5] However, some cases of manganese poisoning have been reported in the literature. Excess manganese in the drinking water is also believed to be the cause of a rare disease endemic in Manchukuo. That manganese may be toxic is also indicated by the reports that 0.5-6.0 grams of manganese per kg of body weight administered daily to rabbits has stunted growth and interfered with bone development.[5]

Whereas acute intoxication involves the respiratory system (manganese pneumonia, nose bleed, nasal congestion); chronic manganese poisoning affects the central nervous system, mainly the midbrain between the cerebellum and the cerebral cortex.[8] The disease causes disorders in mentation, disorientation, impairment of memory and judgment, acute anxiety and even delusions. Exposure to heavy concentrations of dusts or fumes for as little as three months may produce chronic manganese poisoning, but usually cases develop after 1-3 years exposure.[8] The central nervous system is the chief site of damage. If cases are removed from exposure shortly after the appearance of symptoms, some improvement in the patient's condition frequently occurs though there may be some residual disturbances in gait and speech. When well established, however, the disease results in permanent disability.[8]

Plants apparently absorb manganese primarily in the divalent state.[19] Lowering the soil pH or reducing soil aeration by flooding or compaction favors the reduction of manganese to this form and thereby increases its solubility and availability to plants. Heavy fertilization of acid soils without liming (particularly with materials containing chlorides, nitrates, or sulfates) may also increase manganese solubility and availability.

In moderately well-drained soils, manganese toxicity is generally found only if the soil pH is below about 5.5, however, in flooded soils, the reducing conditions produced can result in temporary toxic concentrations of divalent manganese at a pH approaching 7.0. This reduction process is favored by higher soil temperatures. Manganese toxicity in plants is charactertized by marginal chlorosis and cupping at young leaves and speckling of older leaves, which is associated with localized manganese accumulations. Such necrotic spots in barley leaves have been prevented by adding soluble silicon to the nutrient solution. The beneficial effect of silicon was attributed to a redistribution of manganese within the plant, rather than to reduced manganese uptake. In severe cases of manganese toxicity, plant roots turn brown, but this generally occurs only after the tops have been noticeably injured.[19]

Manganese toxicity can be reduced by increasing the concentrations of other cations (calcium, zinc, copper, and magnesium) that compete for absorption by plants in the growth medium. In addition some elements appear to interact with manganese inside the plant and thereby affect its toxicity. Manganese toxicity has been associated with iron deficiency in pineapple. The addition of iron salts to the growth medium can reduce manganese toxicity in tobacco, rice and clover.[19]

C. Environmental Properties

As a contaminant in water and soil the provisional limit for manganese dioxide is 0.05 ppm.[6]

Like iron, manganese occurs in the divalent and trivalent form.[5] The chlorides, nitrates and sulfates are highly soluble in water; but the oxides, carbonates, and hydroxides are only sparingly soluble. For this reason, manganic or manganous ions are seldom present in natural surface waters in concentrations above 1.0 mg/liter. In ground water subject to reducing conditions, manganese can be leached from the soil and occur in high concentrations. Manganese frequently accompanies iron in such ground waters and in the literature the two are often linked together.[5]

Manganese occurs in the atmosphere mainly as manganese oxide, which interacts rapidly with other pollutants, such as sulfur dioxide and nitrogen dioxide, to form water-soluble manganese compounds.[8]

Marine organisms are capable of concentrating manganese in their bodies to many times above the concentration in seawater; manganese enrichment factors for shellfish, compared with their marine environment, range from 1,100 to 13,500; and for algae, as 60,000 (from 0.002 mg/kg in seawater to 120 mg/kg in the algae). Manganese concentration factors of up to 100,000 times an initial seawater concentration of 0.001 ppm for marine plants, and a manganese concentration factor of up to 100 times for fish have been reported.[19] Similarly concentration factors for man and terrestrial mammals are 3-4 and 10, respectively.[19]

The availability of manganese to plants is affected by numerous soil characteristics, including the concentration of total or easily reducible manganese in soil parent materials, concentrations of other cations and total salts, pH, cation-exchange capacity, drainage, organic matter content, temperature, compaction, and microbial activity. Small changes or inherent differences in these soil characteristics can determine whether the soil content of available manganese will be deficient, adequate, or toxic for a given crop.[19]

D. Radioactive Properties: None

Mercury and Its Compounds

A. Physical/Chemical Properties

Elemental Mercury (Hg)

Mercury (at.wt. 200.59, m.p. -38.89°C, b.p. 356.9°C, v.p. 1mm at 126.2°C, d^{20}_{4} 13.5939)[9] is a silver-white, heavy, mobile, liquid metal which is slightly volatile at ordinary temperatures[1]; with every degree rise in temperature its volatility rises 10 percent.[8] It is insoluble in hydrochloric acid, water, alcohol and ether but is soluble in sulfuric acid upon boiling and readily soluble in nitric acid.[4] Mercury has an extremely high surface tension engendering it with unique rheological behavior.[4] This metal is converted by heating with concentrated H_2SO_4 into mercurous or mercuric sulfate (depending on the excess of the acid at the time of heating).[1] When pure, mercury does not tarnish on exposure to air at ordinary temperature, but when heated to near the boiling point, mercury slowly oxidizes to HgO.[1]

Mercuric Chloride ($HgCl_2$)

Mercuric chloride (m.w. 271.52, d. 5.4, m.p. 277°C, b.p. 302°C[9]) is a white substance which occurs as crystals, granules, or powder.[1] $HgCl_2$ volatilizes unchanged at about 300°C, it is slightly volatile at 25°C and appreciably so at 100°C.[1] Its solubility in water is 69.0 g/liter at 20°C and 480 g/liter at 100°C[9]; the pH of a .2 molar aqueous solution is 2.2.[1] $HgCl_2$ is amphoteric; therefore its solubility is increased by HCl or alkali chlorides. $HgCl_2$ is soluble in alcohol (very soluble in hot alcohol), benzene, ether, glycerol and acetic acid.[1]

Mercuric Oxide (HgO)

Mercuric oxide (m.w. 216.61, d. 11.14, m.p.(dec) 500°C[1]) is soluble in water as follows: 53 mg/liter at 25°C, 395 mg/liter at 100°C.[9] It exists in two forms, red and yellow.

Red mercuric oxide is a heavy, bright red or orange-red, odorless, crystalline powder or scales. Its color is yellow when finely powdered. HgO (red) decomposes into its elements when exposed to light[1] or when heated to 500°C[3]. At 400°C it becomes dark red-black but becomes red again upon cooling. Amphoteric HgO (red) is soluble in dilute HCl or HNO_3 and solutions of alkali cyanides or alkali iodides; it is slowly soluble in alkali bromides, and insoluble in alcohol.[1]

Yellow mercuric oxide is an odorless, amorphous yellow to orange-yellow powder[3] which turns red when heated; the yellow color returns after cooling[1] which decomposes to its elements at 500°C.[3] It is stable in air but turns dark upon exposure to light.[4] Other physical properties and solubilities are the same as those of the red form, but the yellow form is more reactive because the particles are more finely divided.[1]

Mercurous Sulfate (Hg_2SO_4)

Mercurous sulfate (m.w. 497.24, d. 7.57) is a white to yellow crystalline powder which decomposes when heated[4] and becomes gray on exposure to light.[1] Hg_2SO_4 is soluble in nitric and sulfuric acids; its solubility in water is 600 mg/liter at 25°C and 900 mg/liter at 100°C.[9]

Mercuric Sulfide (HgS)

Mercuric sulfide (m.w. 232.68, sp.gr. 8.06-8.12, m.p.(sub) 583.5°C)[9] precipitates out as a bright scarlet-red powder or hexagonal red crystals which blacken on exposure to light, particularly in the presence of water or alkali hydroxides.[1] When it is ignited in air it decomposes into elemental Hg and sulfur, the latter burning to SO_2.[1] Mercuric sulfide is practically insoluble in water (at 18°C, solubility is 1.25×10^{-5} g/liter) and alcohol but is soluble in aqua regia with separation of sulfur in warm hydriodic acid with the evolution of H_2S.[1]

Other Mercury Salts

When heated with Na_2CO_3, mercury salts yield metallic Hg and are reduced to metal by H_2O_2 in the presence of alkali hydroxide.[1] Soluble ionized mercuric salts give a yellow precipitate of HgO with NaOH and a red precipitate of HgI_2 with alkali iodide.[1] Mercurous salts give a black precipitate with alkali hydroxides and a white precipitate of calomel with HCl or soluble chlorides. They are slowly decomposed by sunlight.[1]

B. Biological Properties

General

Mercury is a cumulative protoplasmic poison; after absorption it circulates in the blood and is stored in the liver, kidneys, spleen and bone. It is eliminated in the urine, feces, sweat, saliva and milk. Adequate evidence now exists to ascribe differences among various forms of mercury poisoning to differences in the biological distribution and excretion of the causitive agents and their metabolites.[2] Respiratory exposure to mercury vapor results in the retention of high initial concentrations in the lungs. A large proportion of this lung burden is absorbed and gradually cleared. Transiently, high concentrations are said to exist in the brain and may be related to the high incidence of central nervous system signs seen after this type of exposure. The kidneys, however, eventually accumulate the greatest proportion of the total body burden.[2]

Mercury poisoning may be acute or chronic with the latter being the more prevalent of the two types. Symptoms and signs involving the central nervous system are these most commonly seen in chronic poisonings of inorganic mercury, the principal features of which are tremors and psychological disturbances.[2] Intoxication from mercury vapor or from absorption of mercuric salts may be due, in both cases, to the action of the mercuric ion.[6] Metallic mercury vapor is able to diffuse much more extensively into the blood cells and various tissues than inorganic mercury salts, but once distributed, most of it is oxidized to the mercuric form. In most cases of industrial exposure to mercurials, symptoms of mercury poisoning were observed only among workers who had been exposed to mercury levels above 100 micrograms/M^3 in air.[6]

Elemental Mercury

Metallic mercury constitutes a special case in the toxicology of mercury compounds since dangerous symptoms are recognized only after inhalation or prolonged skin contact.[2] In respiratory exposures, Hg vapor diffuses through the alveolar membrane and reaches the brain where it interferes with coordination; severe non-productive cough and dyspnea sometimes precede symptoms of systemic mercury poisoning.[2] Inhalation of mercury in concentrations of 1200-8500 micrograms/M^3 in air results in acute intoxication, affecting primarily the digestive system and kidneys, and is characterized by a metallic taste, nausea, abdominal pain, vomiting, diarrhea, headache and sometimes albuminuria.[6] After a few days the salivary glands swell, stomatitis and gingivitis develop, and a dark line of mercuric sulfide forms on the inflamed gums. Death as a result of extreme exhaustion frequently occurs with poisoning of this degree of severity.[6]

Inorganic Mercury

The action of inorganic mercury differs considerably from that of organic methyl mercury.[8] Inorganic mercury usually settles in and damages the liver and kidneys, especially the kidney tubules (the portion of the nephron involved in reabsorption of vital agents from the urine). In the small intestines it accounts for diarrhea. Mercury vapor diffuses readily through the alveolar membrane and reaches the brain, where it interferes with coordination.[8]

Organic Mercury

The discovery of the facile, biological conversion of mercury and its compounds to methyl mercury have brought into question the wisdom of any large scale use of mercury and its inorganic and organic compounds.[6]

Organic mercury compounds may enter the body by inhalation, skin absorption or ingestion.[6] There is evidence that inhalation of organic mercury vapor and aerosols may be more detrimental than the other means of entry since absorption through the respiratory tract leads to a higher rate of accumulation of mercury in the brain.[6]

The toxicologic effects of organomercurials are strongly influenced by the nature of the organic portion of the molecule.[6] Short chain alkyl mercury compounds (e.g. methyl and ethyl mercury) are relatively stable in the body and may circulate for a long time unchanged in the blood; methyl mercury has a biological half-life in man of about 70 days. The stability of the alkyl mercurials, particularly methyl mercury, favors their accumulation in the body where they are found principally in the brain. Thus, more than 98 percent of the mercury found in the brain is in the form of methyl mercury.[6]

Aromatic mercury compounds, methoxyalkyl mercurials and most other organic mercury compounds are degraded to inorganic mercury in the body.[6] Therefore, the physiological and toxicological behavior of the nonalkyl organomercurials resembles that of inorganic mercury compounds, with preferential accumulation in the kidneys and more rapid excretion than the short chain alkyl analogs.[6]

The symptomatology of acute and chronic poisoning from methyl and ethyl mercury is similar; including numbness and tingling of the lips or hands and feet, ataxia, disturbances of speech, concentric constriction of the visual fields, impairment of hearing, and emotional disturbances.[6] With severe intoxication the symptoms are irreversible. Children born to mothers with exposure to large amounts of methyl mercury exhibited mental retardation and also cerebral palsy with convulsions.[6]

Because so few cases of toxicity have appeared from phenyl mercurials exposure, even to high levels in air over a period of years, it is apparent that these compounds are low in toxicity relative to other forms of mercury.[6] Clinical and experimental evidence suggests that a similar conclusion is applicable to methoxyethyl compounds.

Toxicity of Hg Compounds Towards Aquatic & Terrestrial Life

The lethal concentrations of mercury compounds for various aquatic organisms[6] are summarized as follows. For mercuric chloride, the lethal concentrations in ppb are: *E. coli* (bacteria), 200; *Schendismus sp.* (phytoplankton), 30; *Microregma sp.* (protozoa), 150; *Daphnia magna* (zooplankton), 6; *Marinogammarus marinus* (amphipod), 100; *Polycelis nigra* (flatworm), 270; Bivalve larvae (Mollusca), 27; Stickleback (fish), 4-20; Guppy (fish), 20; Eel (fish), 27; Rainbow trout (fish), 9200.[6] The lethal dose of mercuric chloride for rats is 37 mg/kg body weight.[7]

For mercuric nitrate, the lethal concentrations in ppb are: Guppy, 20; Stickleback, 20; *Mericierella enigmatica* (polychaete), 1000; *Mesospheroma oregonesis* (isopod), 15. The lethal dose for mice is 4 mg/kg body weight.[6]

No toxicity data are available for Hg, $HgSO_4$ or mercuric diammonium chloride, as mercuric sulfate decomposes in cold water into a yellow insoluble basic sulfate and free H_2SO_4, and both Hg and mercuric diammonium chloride are insoluble in cold water. It is to be noted however, that Hg and all inorganic Hg compounds discharged into the aquatic environment could eventually be biologically converted into the more toxic methyl Hg by anerobic microorganisms, which can then be taken up by living aquatic organisms.[6]

C. Environmental Properties

The U. S. Drinking Water Standards for Mercury & Compounds is summarized in the table below.

U.S. Drinking Water Standards for Mercury[23]

Contaminant in H2O and Soil	Provisional Limits
Mercury	0.005 ppm
Mercuric Chloride	0.005 ppm as Hg
Mercuric Nitrate	0.005 ppm as Hg
Mercuric Sulfate	0.005 ppm as Hg
Mercuric Diammonium Chloride	0.005 ppm as Hg

Through the food chain mercury becomes more concentrated as it is taken up by its various links; mercury penetrates the surface of plankton by passive absorption.[8] In contrast, fish take up methyl mercury both through consumption of food, mainly plankton, and through their gills. Fish that breathe faster and eat more than other species, such as the tuna, concentrate more mercury in their bodies during their lifetime than other fish. The older the fish, the greater is the mercury concentration in its body. The metal accumulates in its body fats. A long retention time in some fish (mercury's half-life is 200 days) accounts for added accumulation. Birds that eat fish concentrate even more mercury in their body. Whales and seals have been found to contain very high levels of mercury.[8]

A terrestrial bioaccumulation of mercury also occurs. Mercury is accumulated by growing plants, it is absorbed through leaves and roots and is subsequently transmitted to the remainder of the plant.[8] Rodents and ungulates accumulate mercury from the plants, and carnivores feeding on these animals accumulate even more mercury. Therefore, the organisms at the top of the food chain tend to accumulate the greatest amounts of mercury.

D. Radioactive Properties: None

Methyl Alcohol (CH_3OH)

A. Physical/Chemical Properties

Methanol (m.w. 32.04, m.p. -97.8°C, b.p. 64.5°C, flash point 12°C, d^{20}_{20} .8100)[9] is a clear, colorless, highly polar, mobile liquid.[1] It has a slight alcoholic odor when pure; crude methanol may have a repulsive, pungent odor. Methanol is flammable; it burns with a non-luminous, bluish flame. The alcohol is miscible with water, ethanol, ether, benzene, ketones and most other organic solvents. Methanol forms azeotropes with many compounds.[1]

B. Biological Properties

Methyl alcohol is readily absorbed from the gastro-intestinal and respiratory tracts.[2] Once absorbed methanol is eliminated so slowly that it can be regarded as a cumulative poison.[6] It is detoxified in the body by oxidation to formaldehyde and formic acid, both of which are toxic. As little as two teaspoonfuls is considered toxic if ingested.[2] The fatal dose in man lies between 2-8 oz.; this range implies a high variation in individual susceptibility.[2] Death may be prompt, but it is usually delayed for several days and the mortality rate is high. The prognosis improves if treatment is instituted before visual disturbances appear.[2] Though single exposures to fumes may cause no harmful effect, daily exposure may result in the accumulation of sufficient methyl alcohol in the body to cause illness.

The symptoms of methyl alcohol poisoning result from a combination of factors of which a characteristic metabolic acidosis appears to be the trigger.[2] Central nervous depression is due partly to this acidosis and partly to cerebral edema. Acidosis is the result of methanol oxidation to formic acid which accumulates and reduces severely the body's alkali reserve. For unknown reasons, other organic acids including lactic acid also tend to accumulate. The severity of essentially all symptoms in methanol poisoning is said to be proportional to the intensity of this delayed acidosis. Visual disturbances, which are the most distinctive aspect of methanol poisoning in man, may become evident soon after the severe phase begins. The ocular lesion, which involves chiefly the ganglion cells of the retina, is a destructive inflammation followed by atrophy. In the acute phase the retina is congested and edematous, and the edges of the optic disk may be blurred. The result is bilateral blindness, which is usually permanent unless treatment is prompt and energetic. It is generally agreed that metabolically formed formaldehyde is responsible for the ocular lesions in methyl alcohol poisoning. Since ocular damage has yet to be reported in cases of formaldehyde poisoning, it would appear that formaldehyde must be generated at the site of the lesion to produce damage.

Ethyl alcohol, when consumed at the same time as methanol, prolongs the latent period before toxic symptoms appear.[2] It also has been observed that even severe symptoms of methanol poisoning are alleviated by the ingestion of ethanol; and for this reason the recommended treatment includes ethanol in small quantities. The mechanism of this protection lies in the ability of ethyl alcohol to inhibit the metabolic oxidation of methanol, even though this rate is inherently slow. In rats, methanol oxidation requires liver catalase which is inhibited by ethanol.

Although the distribution of methanol in the body has been reported to parallel closely that of ethanol, which in turn is distributed in proportion to the water content of various tissues, some evidence indicates that methanol may be re-excreted into the stomach over periods of several days following ingestion.[2]

Although for human consumption methanol is very toxic, and small amounts of it will lead to blindness and 10 mls. has caused death, aquatic life has a greater tolerance of this substance.[5] Trout withstand 10,000 mg/liter in tap water for two hours without apparent injury; but in distilled water with 250 mg/liter goldfish died in 11-15 hours. The same effect was noted with ethyl alcohol. For fingerling trout in natural waters, up to 8100 mg/liter of methyl alcohol had no harmful effects in 24 hours.

C. Environmental Properties

The water quality standard for methanol is 13.0 mg/liter.[6]

Methanol can be biodegraded very rapidly by unacclimated activated sludges and is very susceptible to biological attack in lakes and streams. This is due in part to the fact that methanol and most alcohols are either naturally occurring or are normal components of sewage. Thus the best method of disposal is via municipal sewage treatment plants, provided the rate of discharge is uniform.[6]

D. Radioactive Properties: None

Nickel and Its Compounds

A. Physical/Chemical Properties

Elemental Nickel (Ni)

Elemental nickel (at.no. 28, m.w. 58.71, d. 8.908, m.p. 1453°C, b.p. 2732°C, v.p. 1mm at 1810°C)[9] is a hard, lustrous, silver-grey ferromagnetic metal which crystallizes in face-centered cubes.[1] Its electrical resistivity is 6.844 microhms-cm at 20°C.[1] Nickel is malleable and is readily fabricated by hot- and cold-working.[4] It is corrosion resistant at ordinary temperatures, and burns in oxygen forming NiO. The solubility of elemental nickel in pure water at 20°C is 12.7 mg/liter;[10] it is soluble in dilute nitric acid, slightly soluble in hydrochloric and sulfuric acids, and insoluble in ammonia and strong alkalis.[4]

Nickel Hydroxide ($Ni(OH)_2 \cdot nH_2O$)

Nickelous hydroxide (m.w. 92.7, d.4.1, m.p.(dec) 230°C)[9] is composed of light green crystals[3] or is an amorphous apple-green powder.[1] When ignited in air at about 400°C nickelous hydroxide absorbs oxygen and is converted to black nickelic oxide (Ni_2O_3).[1] $Ni(OH)_2$ is soluble in dilute acids and ammonia.[1] Its solubility in water is pH dependent. At a pH of 7, the solubility of $Ni(OH)_2$ is about 135 mg/liter. Solubility decreases as pH increases until pH 10.3, the pH at which $Ni(OH)_2$ is least soluble [11.7×10^{-4} mg/liter (theoretical value)]; above pH 10.3 the solubility increases.[18] The solubility of $Ni(OH)_2$ increases the pH in acidic solutions, and is approximately two orders of magnitude more soluble in water at pH 5 that at pH 7.[18] Other ions in solution affect the solubility of $Ni(OH)_2$. In HCl solutions solubility is decreased by about a factor of ten. In H_2SO_4 solutions the solubility is increased by a factor of 5.[18]

B. Biological Properties

Nickel occurs naturally in the blood in two forms: an ultrafilterable fraction and a protein bound fraction, which together account for 87 to 89 percent of the nickel in man.[16] A dietary requirement for Ni has not been determined. Nickel ions can replace calcium ions in the generation of action potentials in muscle, but the duration of the potential is increased.[16]

Nickel and its compounds in high doses have produced cancer of the sinuses and of the lungs in nickel workers in Wales and Ontario.[8] Furnace workers with more than three years of exposure had a death rate 200 times higher than expected. The disease may not develop for 22 years after exposure. However, nickel cannot be considered the exclusive cause of cancer in these cases because of the simultaneous presence in the atmosphere of other air-borne poisons, particularly arsenic and fluoride. Nor has it been determined to what extent the population near such establishments has been affected by the metal.[8]

Partly because of local astringent and irritant actions, nickel salts act as emetics when swallowed (but also by other routes).[2] As with other irritant-emetics, the lethal dose is presumed to vary widely. Although absorption of nickel and most of its salts from the intestines is poor, sufficient quantities are absorbed to cause systemic responses. These include capillary damage (especially in the brain and adrenals), renal injury, myocardial weakness, and central nervous depression. Pulmonary effects are predominant after a respiratory exposure to gaseous nickel carbonyl.[2] Injestion of large doses of Ni, as a Ni compound (1-3 mg/kg body weight), has been shown to cause internal disorders, convulsions and asphyxia in dogs.[3]

Nickel dermatitis can be induced in humans through contact with nickel-plated articles, industrial exposures to nickelous dusts or baths or internal exposure to nickel.[16] The symptoms compose two levels: 1) a simple dermatitis at the area of contact, the typical "nickel itch", consisting of burning and itching of the exposed skin. There is marked variation on individual susceptibility to the dermatitis. It occurs more frequently under conditions of high temperature and humidity when the skin is moist, and chiefly affects the hands and arms; and 2) a chronic eczematous reaction, in which erythema occurs, and later nodules, which may eventually form pustules, appear in the web of the fingers and the forearm.[16]

In many green plants, degree of absorptions of Ni by the roots appears to be dependent upon the soil pH.[16] Raising the pH of serpentine or high nickel solids by the addition of lime usually somewhat alleviates the toxic effects of nickel. The excessive absorption of nickel is thought to reduce the cation exchange capacity of roots in such diverse plants as oats, beans, peas, sunflowers, and tomatoes.[16] Nickel is extremely toxic to citrus plants.[5] It is found in many soils in California, generally in insoluble form but excessive acidification of such soil may render the nickel compounds soluble, causing severe injury or death of plants.[5]

C. Environmental Properties

The provisional limit in water and soil for nickel and its compounds is 0.05 mg/liter.[6]

Little information concerning accumulation in organisms, magnification in food webs and mechanisms of transport throughout the environment is available for nickel and its compounds. The biomagnification phenomena which involves most heavy metals appears to be effective for nickel as well, with the major exception that plants are so sensitive to Ni that relatively little is accumulated before its toxic effects result in the death of the plant.

D. Radioactive Properties: None

Niobium and Its Compounds

A. Physical/Chemical Properties

Elemental Niobium (Nb)

Niobium (a.w. 92.906, d. 8.57, m.p. 2468±10°C, b.p. 4927°C)[9] is a gray or silvery, ductile metal which does not tarnish or oxidize at room temperature; it reacts with oxygen and halogens only when heated.[4] It is not attacked by nitric acid up to 100°C, but vigorously attacked by a mixture of nitric and hydrofluoric acids and by aqua regia but it is attacked by alkaline solutions to some extent at all temperatures.[4]

Niobium Pentachloride ($NbCl_5$)

Niobium pentachloride (m.w. 270.17, d. 2.75, m.p. 204.7°C, b.p. 254°C)[9] exists as a yellow, crystalline, deliquescent solid which decomposes in moist air with the evolution of hydrogen chloride fumes.[4] This niobium salt is soluble in alcohol, ether, carbon tetrachloride and sulfuric acid.[4]

Niobium Pentoxide (Nb_2O_5)

Niobium pentoxide (m.w. 265.81, d. 4.47, m.p. 1460°C)[9] occurs as white, orthorhombic crystals which are insoluble in water but soluble in hydrogen fluoride, fused potassium hydrogen sulfate, or carbonates or hydroxides of the alkali metals.[3]

Niobium Pentoxide Hydrate ($Nb_3O_5 \cdot xH_2O$)

This hydrated niobium salt is soluble in concentrated H_2SO_4, concentrated HCl, HF and alkalis; it is insoluble in NH_3.[9]

B. Biological Properties

There is to date little data available with regard to the toxicity of niobium and its compounds towards humans. The inhalation of niobium nitride has been reported to precipitate gradual reactive changes in the cells of the alveolar epithelium and connective tissues of lymphatic tracts of the lungs. The presence of high concentrations of the substance as dust in the air causes a considerable cellular proliferation with the development of pneumosclerotic foci. The maximum permissable concentration of niobium nitride in the air is suggested to be set at a level of 10 mg/m^3.[24]

Limited animal experiments show high toxicity for some salts of niobium[3] but low oral toxicity for niobium pentachloride.[1] Effects seen have been attributed to enzyme inhibition.[1]

C. Environmental Properties: No data

D. Radioactive Properties: None

Phosphorus and Its Compounds

A. Physical/Chemical Properties

Elemental Phosphorus (P4)

Elemental phosphorus (a.w. 30.975) exists in three allotropic forms: white, black and red.[1]

White (yellow) phosphorus (m.p. 44.1°C, b.p. 280°C, d(solid, 20°C) 1.82, d(liquid, 44.5°C) 1.745) is a colorless or yellowish, transparent, wax-like crystalline solid which darkens on exposure to light.[1] This allotrope sulbimes in vacuo at ordinary temperatures when exposed to light. When it is exposed to air in the dark, it emits a greenish light and gives off white fumes. Its solubility in water is 3.3333 mg/liter in absolute alcohol, 2500 mg/liter and in absolute ether, 9800 mg/liter. White phosphorus is also soluble in chloroform (25,000 mg/liter), benzene (28,571 mg/liter, and is very soluble in carbon disulfide (1.25 x 10^6 mg/liter). One gram of phosphorus dissolves in 80 ml. of olive oil, 60 ml. of oil of turpentine, and about 100 ml. of almond oil. It ignites at about 30°C in moist air; the ignition temperature is higher when the air is dry. White phosphorus combines directly with the halogens to form tri- or penta- halides; it combines with sulfur to form sulfides. This allotrope reacts with several metals to form phosphides and yields orthophosphoric acid when treated with nitric acid. It reacts with alkali hydroxides with the formation of phosphine and sodium hypophosphite.[1]

Black phosphorus (d. 2.25-2.69)[9] is a black crystalline or amorphous solid resembling graphite in texture.[1] It is produced from the white modification under high pressures. It does not ignite spontaneously as does the white allotrope. It is insoluble in organic solvents.[1]

Red phosphorus (d. 2.34, triple pt. at 589.5°C, sublimes at 416°C)[9] a violet-red, amorphous or crystalline powder, is obtained from white phosphorus by heating at 240°C with a catalyst.[1] It has high electrical resistivity; it is much less reactive than white phosphorus . Red phosphorus properties are intermediate between those of the white and black forms. The red allotrope is insoluble in organic solvents and only very slightly soluble in water. It is soluble in phosphorus tribromide and absolute alcohol. Red phosphorus catches fire when heated in air to about 200°C and burns with the formation of the pentoxide. If in contact with $KClO_3$, $KMnO_4$, peroxides and other oxidizing agents, explosicns may result.[1]

Phosphorus Pentasulfide (P_2S_5)

Phosphorus pentasulfide (m.w. 222.29, d. 2.03, m.p. 280°C, b.p. 523°C)[9] is composed of light-yellow or greenish-yellow deliquescent crystalline masses with an odor similar to that of hydrogen sulfide.[4] P_2S_5 is decomposed by water forming H_3PO_4, SO_2 and H_2S.[2] It is soluble in carbon disulfide, in aqueous solutions of alkali hydroxides[4]; its solubility in CS_2 is 2200 mg/liter.[9] In air it forms phosphorus pentoxide which is a strong irritant.[1]

Phosphorus Sesquisulfide (Tetraphosphorus Trisulfide) (P_4S_3)

P_4S_3 (m.p. 172°C, b.p. 407.8°C, d. 2.0)[9] exists as a yellowish-green crystalline mass which is soluble in carbon disulfide but is insoluble in cold water[4] and is decomposed by hot water, yielding H_2S.[1] Its solubility in carbon disulfide at 20°C is about 60 percent (w/w).[1] Phosphorus sesquisulfide is soluble in benzene (111.1 g[30]/liter)[9] and similar hydrocarbons. Phosphorus sesquisulfide is considered dangerous because when heated it emits highly toxic fumes of oxides of phosphorus and sulfur.[3]

B. Biological Properties

Phosphorus

Phosphorus is a general protoplasmic poison that is slowly absorbed through the gastrointestinal and respiratory mucosae.[2] Its toxicity is enhanced when the element is dissolved in solvents such as alcohol or perhaps digestible fats and oils like castor oil. Liquid petroleum, however, retards absorption and decreases phosphorus toxicity. Finely divided particles and emulsions are more toxic than coarse grained preparations, and bile salts are said to be important for phosphorus absorption. Perhaps because of the water content and the low oxygen tension, particles of elemental phosphorus are relatively stable for long periods of time in the alimentary tract. The free element, however, is thought to be the toxic form in tissues. Some phosphorous is thought to be slowly oxidized to harmless acids, which are gradually excreted by the kidneys.[2]

The acute fatal dose of phosphorus for an adult is between 50-100 mg or approximately 1 mg/kg body weight.[2] Recovery, however, has occurred after 0.8 and 1.5 grams. The prognosis for phosphorus poisoning is generally poor, and even in modern times the fatality rate is about 50 percent. The classical picture of acute P_4 poisoning develops in three stages. Gastrointestinal symptoms occurring shortly after ingestion arise from local irritation, but unlike the response to a truly corrosive poison, the effects may not be immediately evident and sometimes are so mild as to escape recognition. Vomiting is almost always present; early hematemesis may reflect gastric erosion, whereas late hematemesis usually indicates a depression of plasma prothrombin. Secondary to hepatic damage, "explosion of smoke from the mouth" probably describes phosphorus fumes, and vomitus and feces may be luminescent or fuming. Other symptoms in this period are secondary to the gastroenteritis or impending vascular collapse. In many cases stage two is a relatively symptom-free period of several days. In the third stage of systemic intoxication, gastrointestinal symptoms are severe. The liver undergoes acute degeneration and fatty infiltration with accompanying metabolic disturbances.

Hemorrhage may occur at many sites because of depletion of clotting factors.[2]

Phosphorus may also act directly to inhibit protein synthesis in the liver.[2] Hypoglycemia is often observed; its early appearance (stage I) is a grave prognostic sign, as is early azotenia, hepatomegaly or toxic delirium.[2]

The long continued absorption of small amounts of phosphorus can result in necrosis of the mandible, commonly referred to as "phossy jaw".[3] Long continual absorption particularly through the lungs, and through the gastrointestinal tract can cause a chronic poisoning (the most common symptom of which is necrosis of the jaw). It can also cause changes in the long bones, and seriously affected bones may become brittle, leading to spontaneous fractures. It is especially hazardous to the eyes and can damage them severely. It also has adverse effects on the teeth. The yellow form of phosphorus when it comes into external contact with the eyes, can cause conjunctivitis with a yellow tint. If the material is inhaled, it can cause photophobia with myosis, dilation of pupils, retinal hemorrhage, congestion of the blood vessels and rarely an optic neuritis.[3]

White phosphorus is highly toxic to fish. The 96 hour LC_{50}'s are less than 50 ppb for all fish studied, and the incipient lethal level is probably less than 1 ppb for most fish. Phosphorus poisoning appears to be accumulative and irreversible, though the cause of mortality has not been determined. The most obvious symptom of phossy water poisoning, other than death of the victim, is the red color acquired by the belly and head of certain fish, particularly herring. White phosphorus can be expected to cause extensive tissue damage wherever it accumulates. Tissues of the gills, kidneys, liver and spleen may undergo substantial disintegration. However, the symptoms of phosphorus intoxication, including death, are not necessarily related to tissue destruction.

Phosphorous Sesquisulfide

The toxicity of P_4S_3 administered orally to rabbits is 100 mg/kg.[7]

Phosphorus Pentasulfide

Phosphorus pentasulfide is only a mild irritant in its pure solid state.[6] It can cause slight skin irritation upon contact and serious irritation to the eyes and mucous membranes. The major hazard associated with phosphorus pentasulfide is a result of the rapid decomposition of P_4S_{10} upon contact with moisture into toxic and flammable hydrogen sulfide (H_2S) and phosphoric acid (H_3PO_4). Phosphorus pentasulfide is also extremely dangerous when heated. The fumes emitted are phosphorus pentoxide which has a recommended TLV of 0.1 mg/m^3 of air, and the oxides of sulfur which are also toxic (TLV of 5 ppm for SO_2). In addition, phosphorus pentasulfide has also been known to react with acids and oxidizing agents to yield the same products as the reaction with water.[6]

C. Environmental Properties

The standard for phosphorus in water and soil is 0.005 mg/liter as P, while the provisional limit for phosphorus pentasulfide in soil or water is 0.05 mg/liter as P.[6]

Phosphorus does not occur free in nature, but is found in the form of phosphates in several minerals and it is a constituent of fertile soil, plants, and the protoplasm, nervous tissue and bones of animal life.[5] It is an essential nutrient for plant and animal growth, and like nitrogen it passes through cycles of decomposition and photosynthesis. It combines directly with oxygen, sulfur, hydrogen, the halides and many metals.[5]

Evidence indicates[13] (a) that high phosphate concentrations are associated with eutrophication of waters manifest in unpleasant algae or other aquatic plant growths when other growth-promoting factors are favorable; (b) that aquatic plant problems develop in reservoirs or other standing waters at phosphate values lower than those critical in flowing streams; (c) that reservoirs and other standing waters will collect phosphates from influent streams and store a portion of these within the consolidated sediments; and (d) that initial concentrations of phosphate that stimulate noxious plant growths vary with other water quality characteristics, producing such growths in one geographical area but not in another.[14]

Critical phosphorus concentrations will vary with other water quality characteristics.[14] Turbidity and other factors in many of the nation's waters negate the algae-producing effects of high phosphorus concentrations when waters are detained in a lake or reservoir, the resultant phosphorus concentration is reduced to some extent over that in influent streams by precipitation or uptake by organisms and subsequent deposition in fecal pellets or the bodies of dead organisms. No recommendation can be made because of the complexity of relationships between phosphate concentrations in water, biological productivity and resulting problems such as odor and filtration difficulties.[14]

Although there are no definite published reports on the kinetics of oxidation of elemental phosphorus in water, it appears that the rate is highly dependent on the degree of dispersion.[15] At concentrations (ca. 10 micrograms/liter) well below the accepted solubility limit of 3 mg/liter with the dissolved oxygen content unspecified, elemental phosphorus disappears by a first order process with a half-life of 2 hours at about 10°C 0.85 hours at 30°C. At concentrations (50-100 mg/liter) well above the solubility limit, with a dissolved oxygen content of 6-7 mg/liter, the same reaction has a half-life of 80 hours at 30°C and 240 hours at 0°C. The relatively small temperature effect combined with the large inverse concentration effect is consistent with a diffusion controlled process. The oxidation of colloidal phosphorus in seawater is reported to be measurably slower than in fresh water, suggesting that the high salt content brings about agglomeration of the phosphorus particles. Thus, rapidly moving fresh water should lose elemental phosphorus faster than quiescent seawater.[15]

White phosphorus is readily taken up by fish and other aquatic organisms directly from the water.[15] Fish may also acquire lethal quantities of elemental phosphorous through the food chain, since the macroinvertebrates studied have a much higher tolerance for white phosphorus than fish. The symptoms of phosphorus intoxication are passed onto brook trout when they are fed muscle tissue from phosphorus -poisoned cod. Furthermore, elemental phosphorus can be passed on to humans, since a considerable portion, 25 percent or more, remains in the muscle of the fish after processing, storage, and cooking.[15]

D. Radioactive Properties: None

Selenium and Its Compounds

A. Chemical/Physical Properties

Elemental Selenium (Se)

Selenium (a.w. 78.96)[9] exists in several allotropic forms: amorphous, crystalline or red, and grey or metallic.[1] The amorphous form (d. 4.28) ranges from a dark red to black powder which is soluble in carbon disulfide, methylene iodide; benzene or quinoline. Only the red allotrope (m.p. 144°C, d. 4.42) has a sharp, well-defined melting point; it boils at 685°C forming dark red vapors.[1] The crystalline/red allotrope's dark red translucent crystals are metastable and change into the grey form on heating. The crystalline/red form is soluble in dilute aqueous caustic alkali solutions, in aqueous potassium cyanide solution and in potassium sulfite solution. It burns in air with a bright blue flame, forming the dioxide and emitting a characteristic odor resembling rotten horse-radish.[1] The red form combines directly with hydrogen and with the halogens (excluding iodine) and is oxidized to selenious acid by nitric acid and to selenic acid by sulfuric acid.[1] It reduces hot aqueous solutions of silver and gold salts with the formation of silver selenide and metallic gold, respectively.[1] The grey or metallic form (m.p. 217°C, d^{20}_{4} 4.81) is the most stable allotrope.[1] Its lustrous grey to black hexagonal crystals are insoluble in water and alcohol; very slightly soluble in carbon disulfide (20 mg/liter) and soluble in ether.[1]

In common with almost all metals, sufficiently fine selenium powder may explode in air to form the water soluble selenium dioxide.[6] Selenium will react with acids to form the highly toxic H_2Se gas.[6]

Ferrous Selenide (FeSe)

Ferrous selenide (m.w. 134.81, d. 6.78) is a black mass with a metallic luster.[1] It is stable in air but decomposes when heated in O_2.[1] It is practically insoluble in water but is soluble in HCl with the evolution of H_2Se.[1]

B. Biological Properties

Selenium dioxide readily dissolves in water producing selenious acid.[16] Intense local irritation and inflammation of the skin and mucous membranes occur upon contact. Selenium dioxide, selenious acid, and selenite may be absorbed through the skin, resulting in internal accumulation. Allergic dermatitis to selenium dioxide may develop, especially in fairheaded people.[16] Sodium thiosulfate is used to treat exposure. Selenium oxychloride is a severe vesicant, capable of producing a third degree burn which is extremely painful and slow to heal. Dimethyl selenide produces acute sore throat and pneumonitis.[16]

Surveys have shown that dental caries rates of permanent teeth were significantly higher in seleniferous areas than in non-seleniferous areas. There is also a tendency for malocclusion and gingivitis in seleniferous areas.[5]

Selenium is transmitted from the mother to the fetus. Reduced reproductive rates and weakened offspring occur in selenium-deficient mothers. Excessive selenium may act as a teratogen. The majority of the evidence indicates that selenium compounds can function as anti-tumor agents rather than carcinogens.[16]

Although elemental selenium has low systemic toxicity, dust or fumes can cause serious irritation of the respiratory tract. Workers exposed to fine elemental dust collect the dust in the upper nasal passages, producing catarrh, nosebleeding, and loss of smell.[16] A few cases of selenium dermatitis have occurred. Exposure to fumes of elemental selenium produces frontal headache, intense irritation of the eyes and nasopharyngeal passages, slight difficulty in breathing, and uvular edema. Exposed workers recovered within three days and no ill effects persisted.

Selenium poisoning occurs naturally among cattle, sheep, horses, pigs and even poultry in both chronic and acute forms.[5] Chronic poisoning of the alkali disease type results from the ingestion of food stuffs (corn, wheat, barley, oats, grasses and hay) containing 10-30 ppm solution.[18] The selenium is predominantly present in the proteins of these feeds. The amount of selenium is related to the availability of soil selenium. The general symptoms of alkali disease include lack of vitality, anemia, stiffness of joints, lameness, roughened coat, loss of hair, and hoof lesions and deformities. Death may occur within two months after a horse is placed in a seleniferous pasture. The heart and liver exhibit the most damage - the heart becomes soft, flabby and atrophied. Fibrosis is evident in the liver and kidneys.[16]

Minute concentrations of selenium appear not to be harmful to fish during an exposure period of several days; however, constant exposure to traces of selenium has caused disturbances of appetite and equilibrium, pathological changes, and even deaths of fish after several weeks.[5] Concentrations considered safe for human beings over a period of weeks have been toxic to fish.

C. Environmental Properties

The drinking water quality standard for selenium and its compounds is 0.01 mg/liter as Se.[6]

Selenium may enter animals in several ways. The predominant route is through ingestion of vegetation containing high levels of selenium. Animals readily absorb inorganic and organic selenium through the small intestine. Monogastric absorption is more efficient than ruminant. 70-80 percent of the selenium is quickly excreted in the urine, breath, perspiration, and bile. The remaining selenium becomes bound or incorporated into the blood and tissue proteins and is only slowly eliminated. Carnivores obtain selenium by eating prey fed on seleniferous forage. Selenium in drinking water is another source. Small amounts of selenium may be inhaled, as animals, plants, and microorganisms all produce volatile selenium compounds.[16]

Soil selenium enters the food chain by plant accumulation. In seleniferous soils, certain species of plants prevail which easily accumulate selenium levels toxic to livestock. In fact, the presence of certain plant species is steadfast evidence of a seleniferous zone. Crop plants grown on such soils, if they themselves survive, may also contain selenium levels poisonous to livestock.[16]

Plants vary in their ability to absorb selenium; the final selenium concentration in the plant will be determined by such factors as the species and age of the plant, the season of the year and the concentration of soluble selenium compounds in the root zone.[5] Cereals and grains concentrate selenium from the soil, the amount depending on the chemical condition of the selenium, the type of crop, and the sulfate content of the soil. High sulfates diminish the uptake of selenium. Plants have been injured by selenium in the soil, however, injury to plants can be reduced or prevented by sulfate ion, when it is present in a concentration about 12 times as high as that of selenium.[5]

The selenium in young soils occurs predominantly in an inorganic form not utilizable by crop plants.[16] Selenium accumulator plants and some bacteria can function as selenium converters, removing the selenium from the soil and returning it in an inorganic form, which can be absorbed by other plants. The established biological valence transformations of selenium are reduction reactions. Selenate, and selenite can be converted to elementary selenium and selenoorganics by plants and microorganisms. Evidence for microbial oxidation of selenium is the lack of buildup of organic selenium compounds in nonsterile soils. However, the oxidative stages in the selenium cycle may be abiotic, as about 80 percent of elementary selenium as dust in moist air is converted to selenium dioxide, which reacts with water to form selenious acid. Selenite is the most unstable form of selenium, and may be readily oxidized to selenate.[16]

Organic selenium and some selenium salts are easily leached from soils, and the selenium content of irrigation waters, springs, and shallow pools may be quite high in seleniferous regions.[16] In alkaline soils, much of the selenium may be trapped by reaction with iron oxides. Iron selenium compounds are quite insoluble under basic conditions, and the selenium available to indicator plants and microorganisms, but not crop plants. Acidification of the soil by microbe action can cause the conversion of insoluble inorganic selenium to soluble forms.[16]

D. Radioactive Properties: None

Silver and Its Compounds

A. Physical/Chemical Properties

Elemental Silver (Ag)

Silver (a.w. 107.87, m.p. 960.5°C, b.p. 2212°C, d. 10.5)[9] is a soft, ductile and malleable, lustrous white solid[4] with a face-centered cubic structure.[1] It resists oxidation, but tarnishes in air through reaction with atmospheric sulfur compounds (sulfur and HS) and ozone.[4] Ag is the best conductor of heat and electricity and is more malleable and ductile than any other metal except gold. This metal is insoluble in water and in most acids; readily soluble in dilute nitric acid, KCN, in hot concentrated sulfuric acid; it is superficially attacked by HCl.[1] In the presence of air or oxygen, silver solubilizes in fused alkali hydroxides and alkali cyanides.[1] Most silver salts are photosensitive.[1]

Silver Chloride (AgCl)

Silver chloride (m.w. 143.32, d. 5.56, m.p. 455°C, b.p. 1550°C) is a white powder with cubic crystals which exists in nature as the mineral cerargyrite. It is soluble in ammonium hydroxide, sodium thiosulfate potassium cyanide[9], concentrated sulfuric acid, potassium bromide[3], concentrated hydrochloric acid, ammonium chloride, mercuric nitrate and silver nitrate[4]; its solubility in water is .89 mg/liter at 10°C[9], 2 mg/liter at 25°C[4] and 21 mg/liter at 100°C[9]; it is insoluble in alcohol and dilute acids[4]. AgCl darkens upon exposure to light and finally turns black, it exists in several modifications differing in conduct toward light and in solubility in various solvents. AgCl can be melted, cast and fabricated like a metal.[3]

Silver Nitrate ($AgNO_3$)(1)(9)(3)(4)

Silver nitrate (m.w. 169.87, d. 4.352, m.p. 212°C, b.p.(dec) 444°C) is a colorless, transparent, tabular, rhombic, crystalline substance which is odorless and has a bitter, caustic metallic taste and which becomes gray or grayish-black on exposure to light in the presence of organic matter or H_2S regardless of presence or absence of light. $AgNO_3$ is a strong oxidizing agent and caustic. It is soluble in ether, glycerin, hot alcohol, ammonia water, and very slightly soluble in absolute alcohol and acetone. Its solubility in water is 1220 g/liter at 0°C and 9520 at 190°C; the resulting pH of a saturated aqueous solution of $AgNO_3$ is about 6.

Silver Oxide (Ag_2O)

Silver oxide (m.w. 231.74, d. 7.143, m.p. (dec) 300°C) is a heavy, odorless, brown-black cubic powder with a metallic taste which breaks up into its constituents upon exposure to sunlight; moist Ag_2O absorbs carbon dioxide. It is soluble in potassium cyanide solution, ammonium hydroxide, acids e.g. dilute nitric acid, and sodium thiosulfate solution; it is virtually insoluble in alcohol. The solubility of Ag_2O in water is 13 mg/liter at 20°C and 53 mg/liter at 80°C. Its solubility is pH dependent. As pH decreases solubility increases such that below pH 5, Ag_2O is freely soluble. As pH increases above pH 7 solubility decreases to pH 12, the pH at which Ag_2O is least soluble (.92 mg/liter). Above pH 12 solubility increases.

Silver Hydroxide (AgOH)

Almost no information is available on the properties of silver hydroxide. Because of its high solubility in water and the preferential formation of Ag_2O (discussed previously), it is virtually nonexistent.

B. Biological Properties

Although the essentially insoluble chloride, bromide, iodide, and oxide of silver are generally non-irritating and relatively benign, some silver salts have been found to be irritating to skin and mucous membranes.[2] The ingestion of corrosive silver nitrate ($AgNO_3$) has been responsible for most cases of acute silver poisoning. The symptoms are those of a severe gastroenteritis and shock, with vertigo, coma, convulsions, and death.[2] Chronic exposure to silver salts may cause argyrism, solely of cosmetic concern.[2] Argyrism is characterized by a greyish-blue discoloration of the skin.

Silver poisoning is treated like acute copper poisoning, except that gastric lavage should be performed with sodium chloride solutions.[2] Apparently BAL has not received a therapeutic trial in acute poisoning. In cases of argyria (result of chronic exposure to silver), BAL has been found not to increase the excretion of silver.[2]

C. Environmental Properties

The water quality standard for silver and its compounds is 0.05 mg/liter as Ag.[6]

From silver ores (Ag_2S, AgCl, etc.) silver ions may be leached into ground waters and surface waters, but since many silver salts such as the chloride, sulfide, phosphate and arsenate are insoluble, silver ions cannot be expected to occur in significant concentration in natural waters.[5]

D. Radioactive Properties: None

Strontium Sulfate ($SrSO_4$)

A. Physical/Chemical Properties

Strontium sulfate (m.w. 183.63, m.p. 1605°C, d. 3.96)[9] is a white, odorless, crystalline powder which is appreciably soluble in alkali chloride solutions.[1] Its solubility in water at 17.4°C is 114.3 mg/liter; at 32.3°C is 114.3 mg/liter, and at 2.5°C is 113.3 mg/liter. Strontium sulfate's solubility in 2 percent hydrogen chloride solutions is 1250.0 mg/liter, and 1430.0 mg/liter in 8 percent nitric acid solutions. It is insoluble in alcohol and dilute sulfuric acid.[1]

B. Biological Properties

Strontium is present in plant and animal tissues in trace concentrations, but it occurs in much higher concentrations in bone structures.[5] There is no evidence that strontium is essential for plant nutrition, but there are indications that it is necessary for the growth of animals and especially for calcification of bones and teeth. In humans the strontium content of bones has been given as 120-234 mg/kg in contrast with a tissue concentration of less than 0.1 mg/kg. Toxicologically, no evidence has been uncovered to show that nonradioactive strontium salts taken orally by man or animals produces deleterious action.[5] Its toxicity is probably on the same order of magnitude as calcium since the strontium ion is chemically and biologically similar to it. The oxides and hydroxides of strontium are moderately caustic materials. As with other compounds, the toxicity may be a function of the anion.

The toxicities of a few strontium compounds towards rodents are summarized below.

Toxicological Responses of Rodents to Strontium Compounds[7]

$SrCl_2$:	IVN	rat	LD_{20}:	123 mg/kg
	IVN	mouse	LD_{50}:	148 mg/kg
SrF_2:	IVN	rat	LD_{20}:	625 mg/kg
$SrBr_2$:	ipr	rat	LD_{50}:	1000 mg/kg
	IVN	rat	LD_{50}:	1000 mg/kg

With the advent of nuclear fission and weapons testing, strontium came to the forefront of publicity as one of the inevitable constituents of fall-out.[5] Owing to its long half-life and its tendency to accumulate in bone structure, Sr-90 is ranked second only to Ra-226 as a hazard to human health.

C. Environmental Properties

There are no water quality standards except that for dissolved solids, 250 mg/liter.

From studies utilizing radioactively labelled strontium, it was discovered that crop plants tend to accumulate strontium from soils and water.[5] Plants do not appear to discriminate between calcium and strontium in soil moisture and hence the ratio of these two elements in plant tissue tends to be the same as their ratio in the soil solution. The uptake of strontium by plants can be reduced by adding calcium to the soil or applied water.[5]

Measurements of the uptake of strontium by aquatic macrophytes during 7 days exposure in hard river water containing strontium[5] showed concentration factors varying from 30 to 74 for six species.[5] In soft water, however, watercress had a concentration factor of 200 after 28 days in contrast to 55 in hard water. Other experiments showed concentration factors for watercress in the order of 600 to 800 in soft water (20 mg/liter of $CaCO_3$) and less than 100 in hard water (300 mg/liter of $CaCO_3$). The increase in calcium and magnesium ions appears to militate against the uptake of strontium. For Porphyra, sp. an edible seaweed in South Wales, the concentration factor was only 0.05-0.3.[5]

Planktonic algae have also been shown to concentrate strontium.[5] Concentration factors for algae have been reported at values ranging from 8 to 3060. For marine bacteria, a concentration factor of about 100 has been given.

Strontium concentrates in the flesh, bones, and scales of rudd fish by factors of 2.6, 71 and 209 respectively.[5] For lobsters, concentration factors of 300 in the shell, and 2.0 in the flesh were reported.[5] The probable accumulation factor for goldfish (the whole fish) is 150.[5]

It is evident that the major hazard to humans of strontium and radiostrontium (leached from soils and water contaminated with fallout from nuclear explosions or waste products from nuclear reactors) lies not in direct consumption but in plants and fish that accumulate this element.[5]

D. Radioactive Properties: None

Sulfur Dioxide (SO_2)

A. Physical/Chemical Properties

Sulfur dioxide (m.w. 64.07, b.p. -10°C, m.p. -72.7°C, condenses at -10°C to a colorless liquid, d(gas) 1.5, d(liquid) 1.5)[9] is a colorless gas with a pungent irritating odor detectable at concentrations of about 0.5-0.8 ppm. Under conditions of high humidity (clouds or fog droplets), of sunlight, and in the presence of such particulate catalysts as charcoal, ferric oxide, and graphite, conversion of sulfur dioxide to sulfur trioxide takes place.[8] Sulfur dioxide's solubility in water at 0°C is 228.0 g/liter and at 90PC is 5.8 g/liter.[1] SO_2 is also soluble in chloroform, ether, acetic acid and H_2SO_4.[1]

B. Biological Properties

Sulfur dioxide is a highly irritant gas which is often cited as a dangerous atmospheric constituent in smog areas.[2] Inhalation produces all grades of respiratory tract irritation, sometimes with pulmonary edema. The vapor concentration probably determines the mode of death, for example, suffocation from reflex respiratory arrest (very high concentration), pulmonary edema (moderate concentration), or systemic acidosis (low concentration).[2] There is some indication of individual susceptibility.

The gas is dangerous to the eyes, as it causes irritation and inflammation of the conjunctiva.[3] In moist air or fog, it combines with water to form sulfurous acid, but it is only very slowly oxidized to sulfuric acid. Concentrations of 6-12 ppm cause immediate irritation of the nose and throat, while 0.3-1 ppm can be detected by the average individual possibly by taste rather than by the sense of smell. 3 ppm has an easily noticeable odor and 20 ppm is the least amount which is irritating to the eyes. 10,000 ppm is an irritant to moist areas of the skin within a few minutes of exposure.[3]

Sulfur dioxide chiefly affects the upper respiratory tract and the bronchi.[3] It may cause edema of the lungs or glottis, and can produce respiratory paralysis. More than 90 percent of the inhaled gas is absorbed in the airways above the larynx. The degree of irritation of sulfur dioxide, sulfuric acid, and sulfates to the respiratory tract is dependent largely on their concentration in the atmosphere and the size of the particles. The size that causes most irritation to the respiratory tract is about 1 micron in diameter or slightly less; but even larger sulfuric acid particles, which do not reach the lower airways, induce constriction of bronchi associated with severe coughing as the result of reflex action.

An important feature of the biologic behavior of sulfur oxides is their interaction with other pollutants.[8] Aerosols of soluble salts of iron, manganese or vanadium in concentrations of 0.7 mg/m^3 to 1 mg/m^3 induce a three-fold increase in airway resistance in experimental animals. These substances form droplets in the humid respiratory tract and thus permit solution of sulfur dioxide. Furthermore they are catalytic agents for the oxidation of sulfur dioxide to sulfuric acid. Sulfuric acid mist at 8 mg/m^3 combined with 89 ppm of sulfur dioxide produced greater injury to lungs, greater alterations in respiration, and greater retardation of growth than either one alone.

The combination of sulfur dioxide with hydrogen peroxide (H_2O_2) at concentrations of 0.29 mg/m^3 for five minutes, with particle size of 4.7 microns, induced a synergistic effect.[8] However, when hydrogen peroxide was associated with the same concentration of sulfur dioxide but of reduced particle size (11.8 microns), no potentiating effect occurred.

Inhalation of sulfur dioxide together with fine particles of sodium chloride (0.04 microns in diameter) accounted for greater airway resistance than inhalation of sulfur dioxide alone.[8] However, no such synergism occurred when the size of NaCl particles was increased to 2.5 microns at the same concentrations.

The interaction of particulates with sulfur dioxide in animals is a highly complex process and does not always parallel that in humans.[8] Experiments with normal human volunteers have failed to demonstrate consistent potentiation of the response to sulfur dioxide by sodium chloride particles.[8]

Concentrations of less than 1 ppm of sulfur dioxide are believed to be injurious to plant foliage.[3] Sulfur oxides tend to dry up the plant, which then assumes a light ivory or tan color.[8] The injury to leaves originates and concentrates between their veins. Often the veins themselves begin to bleachout. Grasses, which have two layers of palisade cells, collapse throughout the thickness of their blade. On evergreens, sulfur oxides induce a reddish discoloration either at the tips of the needles or as a band over their entire length; subsequently the dead tissue shrivels up. Sulfuric acid, which is formed in the atmosphere by sulfur oxides (SO_3) in the presence of moisture, produces small necrotic (dead) areas simulating burns. They are surrounded by a black ring with its edges slightly erased.

C. Environmental Properties

In domestic water, sulfur dioxide and sulfites are deleterious primarily in that they lower the pH value and increase corrosivity.[5] By being oxidized and utilizing dissolved oxygen, on the other hand, sulfites may retard corrosion.

The recommended ACGIH's Threshold Limit Value for sulfur dioxide is 5 ppm in air (13 mg/m^3 air) and 0.65 mg/liter in soil and water.[6] About 80 percent of all sulfates constitute particles below two microns in diameter.[8] These particles suspended in the atmosphere account for reduction of visibility, a characteristic feature of sulfur oxide pollution.

D. Radioactive Properties: None

Vanadium Compounds

A. Chemical/Physical Properties

Vanadium Pentoxide (V_2O_5)

Vanadium pentoxide (m.w. 181.88, d. 3.357)[9] is a yellow to red orthorhombic crystalline powder with a melting point of 690°C and which decomposes at approximately 1750°C.[1] This salt of vanadium is soluble in concentrated acids and alkalis, forming vanadates[1]; its solubility in cold water is 8 g/liter.[9] It is insoluble in alcohol.[1] Its acid solutions are reduced by SO_2, Zn + HCl, and by evaporation with HCl.

Vanadium Dichloride (VCl_2)

Vanadium dichloride (m.w. 121.85, d. 3.23, m.p.(subl)@910°C)[9] is comprised of apple-green[4] deliquescent hexagonal plates.[3] It is soluble in alcohol and ether and decomposes in hot water.[4]

Vanadium Trichloride (VCl_3)

Vanadium trichloride (m.w. 157.30, d. 3.00, m.p.(dec) 425°C)[9] is a mass of pink deliquescent crystals which are soluble in absolute alcohol and ether and which decompose upon heating and in water.[4]

Vanadium Tetrachloride (VCl_4)

Vanadium tetrachloride (m.w. 192.75, d. 1.816, m.p. -28 ± 2°C, b.p. 148.5°C)[9] is a reddish brown liquid which is soluble in absolute alcohol and ether.[4] It decomposes slowly to vanadium trichloride and chlorine below 630°C.[4] It is nonflammable.[4] It is soluble in and decomposes in water; it is also soluble in absolute alcohol, ether, acetic acid and chloroform.[9]

Vanadium Tetroxide (V_2O_4)

This blue-black powder (m.w. 165.88, d. 4.339)[9] is derived from V_2O_5 by oxalic acid reduction or carbon reduction.[4] Vanadium tetroxide is soluble in acids and alkalis.[9] It is least soluble in water at pH 5 (25°C) with a solubility of 1.11×10^{-3} g V^{+4}/liter; at pH 9 (25°C), vanadium tetroxide's saturation concentration is 5.09 g V^{+4}/liter.[10]

Other Vanadium Compounds

Salts of vanadium may have valences of 2, 3, 4 and 5. The tetra- and penta- valent salts are generally soluble, but the trivalent salts of fluoride, oxide, and sulfides are insoluble.[5]

B. Biological Properties

Vanadium Pentoxide

Considering the fact that doses of vanadium are rapidly excreted in the urine and the feces, and that complete clearance of the vanadium from the animal usually occurs two to three weeks after vanadium administration has ceased - it appears that the toxic effects of vanadium are primarily exhibited when exposed to it as V_2O_5 dust.

Exposure to vanadium pentoxide in amounts greater than the inhalation tolerance (dust) 0.5, (fume) 0.1 mg/m^3 air generally will induce signs and symptoms of vanadium poisoning which include pallor, greenish-black discoloration of the tongue, paroxysmal cough, conjunctivitis, dyspnea and pain in the chest, bronchitis and radiographic reticulation.[8] The symptoms of exposure to vanadium-laden dusts are generally acute and relief occurs promptly when the irritant is removed. A greenish-black tongue with septic teeth and lingual furring is indicative of vanadium-exposure but not necessarily poisoning. The green color is believed to be due to the deposition of quadrivalent vanadium in the tongue and gums. Systemic poisoning due to over exposure to vanadium dusts can occur. When this happens vanadium alters human metabolism in the following ways:[8]

It inhibits the synthesis of cholesterol, of phospholipids, and of other lipids. Cholesterol, a precursor of the all important adrenocortical hormones, affects a great number of metabolic processes, especially the metabolism of salt, water, minerals and carbohydrates.[8]

It inhibits the formation of cystine, cysteine, and methionine, the three basic sulfur-containing constituents of skin, hair, and nails. Methionine has a sulfur-bound methyl group that enters into the production of adrenalin, choline and creatine.[8]

It interferes with the utilization of iron in the synthesis of hemoglobin. Vanadium also leads to accumulation of serotonin, a crystalline protein and powerful constrictor of blood vessels found chiefly in brain tissue and in the blood.[8]

Vanadium Chlorides

The toxicity of vanadium chlorides administered orally to a rat are as follows:[7]

VCl_2 LD_{50} = 540 mg/kg body weight
VCl_3 LD_{50} = 350 mg/kg body weight
VCl_4 LD_{50} = 160 mg/kg body weight

Vanadium Compounds

The toxicity of vanadium compounds is principally a function of the rate of administration or exposure.[16] Vanadium salts are considered highly toxic in a number of species when given by intravenous or subcutaneous injection. Since most vanadium compounds are poorly absorbed from the gastrointestinal tract, they exhibit a low order of toxicity by the oral route. Most of the orally ingested vanadium is excreted in the feces. Elevated urinary vanadium levels reflect vanadium exposure, and systemic vanadium is rapidly eliminated from the body by the kidneys.

Anionic vanadium is said to be more toxic than cationic.[2] Humans have tolerated 150 mg of vanadium sodium tartrate intramuscularly, and 1-8 mg sodium metavanadate by mouth.[2] Dimercaprol (BAL) exerts no apparent therapeutic benefit in vanadium-poisoning, but calcium disodium edetate and disodium catechol disulfonate are both effective antidotes in animals.[2]

Researchers have found that aerial parts of plants have the lowest vanadium content with the roots having nearly the same content as the soil in which the plant was growing. Though the total supply of trace elements in the soil has a definite bearing on the amount found in the corn plant, the factors which influence the availability of the elements (pH, mineral form, solubility) are more important in determining plant uptake. Plants take up vanadium through the roots especially at acidic pH's.[16] Toxic amounts can be accumulated if insufficient iron is present. Some plants such as *Cleomes spp.* appear to be vanadium-accumulators.[18]

Microbial action plays a strong role in determining the availability of vanadium in the soil. The bi-, tri- and pentavalent states of vanadium make it amenable to microbial attack. Specific autotrophic bacteria oxidize the reduced forms of vanadium to obtain a part or all of their energy for growth and multiplication. Iron-oxidizing bacteria oxidize vanadium in acidic leaching solutions. The oxidized vanadium is more soluble in aqueous solutions and, therefore, capable of transport in ground water. Sulfate-reducing bacteria play an important role in developing the reducing conditions under which the various bacteria operate. Vanadium promotes nitrogen assimilation by soil microorganisms.

Marine plants and invertebrate animals generally, seem to contain vanadium in higher concentrations than terrestrial plants, insects and vertebrates; there exist both marine and terrestrial organisms which tend to accumulate vanadium. Among the marine organisms which do are the tunicates.[16] Apparently they can concentrate vanadium from sea water with their pharyngeal mucous sheath. Vanadium serves as the metallic element in the tunicate blood, existing complexed to pyrrole rings in a structure similar to bile salts.[16]

C. Environmental Properties

Vanadium forms the vanadyl cation (VO) the salts of which are soluble. It also forms the anion vanadate (VO_4). It is likely, therefore, that any vanadium salts occurring in waste water will remain in solution.[5] Lime treatment of vanadate would probably produce $CaHVO_4.2H_2O$ whose solubility is below that of the corresponding phosphate.

The proposed drinking water standard for vanadium is 5.0 mg/liter.[6] The OSHA standard for exposure to vanadium dust and/or fumes is 0.05 mg/m^3.[6]

D. Radioactive Properties: None

Zinc and Its Compounds

A. Physical/Chemical Properties

Elemental Zinc (Zn)

Zinc (a.w. 65.37, m.p. 419.4°C, b.p. 907°C, d. 7.14)[9] is a hexagonal crystalline, lustrous, bluish-white metal which is stable in dry air and becomes covered with a white coating of basic carbonate on exposure to moist air. Pure zinc is very slowly attacked by dilute sulfuric or hydrochloric acid; the presence of a small amount of another metal e.g. copper, tin, lead, accelerates the action of the acids. This metal is slowly soluble in acetic acid and ammonia water; soluble in nitric acid and readily soluble in solutions of fixed alkali hydroxide with the evolution of hydrogen.[1] Zinc foil will ignite in the presence of moisture.

Zinc Chloride ($ZnCl_2$)

Zinc chloride (m.w. 136.29, d. 2.907, m.p. 290°C, b.p. 732°C[3]) is a deliquescent white granular powder composed of cubic crystals, granules, fused pieces or rods. It is extremely soluble in water (4320.0 g/liter at 25°C, 6150.0 g/liter at 100°C[9]) in dilute concentrations some zinc oxychloride (Zn_2OCl_2) is formed.[1] The pH of a concentrated solution of zinc chloride is approximately 4.0.[1] $ZnCl_2$ is very soluble in dilute hydrochloric acid, alcohol, glycerol and acetone.[1]

Zinc Hydroxide ($Zn(OH)_2$)

Zinc hydroxide (m.w. 99.38, d. 3.053, m.p. (dec) 125°C) is a colorless, rhombic powder which is soluble in acids and alkalis, forming zinc salts and zincates ($HZnO_2^-$; ZnO_2^{--}) The water solubility of this amphoteric compound varies with pH; it is least soluble at pH 9.2 (1.04 mg/liter). Solubility increases as pH increases or decreases from 9.2; at pH 7 its solubility is about 2 g/liter; at pH 5 its solubility is about 1000 g/liter.[9]

Zinc Yellow

Zinc yellow is toxic by ingestion.[4] Toxicological properties are due to both zinc and chromium. The toxicological properties due to chromium are discussed under "Chromium and Its Compounds" in this section.

Zinc Oxide (ZnO)

Zinc oxide (m.w. 81.38, d. 5.47, m.p. 1975°C)[4] is a coarse white or grayish, odorless, bitter-tasting powder which absorbs carbon dioxide from the air.[4] It is only slightly soluble in water (1.6 mg/liter at 29°C)[9] but is readily soluble in dilute acetic or mineral acids, in ammonia, ammonium carbonate and fixed alkali hydroxide solutions.[1]

Zinc Yellow

Zinc yellow (m.w. about 3.00) is an odorless, yellow or greenish yellow fine powder which is slightly soluble in water, and soluble in dilute acids, e.g. acetic acid.[1]

B. Biological Properties

Zinc

Zinc is not inherently a toxic element to man, however, when heated, it evolves a fume of zinc oxide which, when inhaled fresh, can cause a disease known as "brass founders' ague" or "brass chills."[3] It is possible for people to become immune to it. However, this immunity can be broken by cessation of exposure of only a few days. Zinc oxide dust has also been known to block the ducts of the sebaceous glands and give rise to a popular pustular eczema in men engaged in packing this compound in barrels.[3] Zinc oxide dust which is not freshly formed is virtually innocuous. There is no cumulative effect to the inhalation of zinc fumes. Fatalities, however, have resulted from lung damage caused by the inhalation of high concentrations of zinc chloride fumes.[8]

Soluble salts of zinc have a harsh metallic taste; small doses can cause nausea and vomiting, while larger doses cause violent vomiting and purging.[3] So far as can be determined, the continued administration of zinc salts in small doses has no effect in man except those of disordered digestion and constipation. Another local manifestation of zinc salts is their caustic effect on the skin leading to ulcerations.[6]

Exposure to zinc chloride fumes can cause damage to the mucous membrane of the nasopharynx and respiratory tract and give rise to a pale grey cyanosis.[3] Chloride, because of its caustic action, can also cause ulceration of the fingers, hands and forearms of those who use it as a flux in soldering. This condition has even been observed in men who handle railway ties which have been impregnated with this material. It is the opinion of some who work with it that it is carcinogenic.[6]

The particle size of zinc oxide and zinc chloride is largely responsible for the type and degree of respiratory symptoms and for their differing toxic effects.[6]

It is towards fish and aquatic organisms that zinc exhibits its greatest toxicity.[5] In soft water, concentrations of zinc ranging from 0.1-1.0 mg/liter have been reported to be lethal, but calcium is antagonistic toward such toxicity. Zinc is thought to exert its toxic action by forming insoluble compounds with the mucous that covers the gills, by damage to the gill epithelium, or possibly as an internal poison. The sensitivity of fish to zinc varies with species, age and condition of the fish, as well as with the physical and chemical characteristics of the water. Some acclimatization to the presence of zinc is possible, and survivors from batches of fish subjected to dissolved zinc have been less susceptible to additional toxic concentrations than fish not previously exposed. It has also been observed that the effects of zinc poisoning may not become apparent immediately, so that fish removed from zinc-contaminated to zinc-free water (after 4-6 hours of exposure to zinc) may die 48 hours later.[5]

The presence of copper appears to have a synergistic effect on the toxicity of zinc.[5] There is little toxic action of zinc precipitated from solution in alkaline water, almost all of the toxicity is attributable to the zinc remaining in solution.[5] They also showed that the toxicity of zinc salts to sticklebacks in soft water is reduced by the addition of calcium carbonate; hence the calcium ion rather than the carbonate ion appears to be the antagonistic factor.[5]

The toxicity of zinc salts is increased at lower concentrations of dissolved oxygen in about the same proportion as for lead, copper and phenols, e.g. the lethal concentration at 60 percent saturation of dissolved oxygen is only about 0.85 that at 100 percent saturation.[5]

Zinc has a toxic effect towards protozoa and bacteria, but not nearly as pronounced as copper.[5] As little as 0.1 mg/liter of zinc will have an effect upon biochemical oxygen demand and 62.5 mg/liter zinc will cause a 50 percent drop in the 5-day BOD. In concentrations up to 1.0 mg/liter zinc is reported to stimulate nitrification, but 10 mg/liter is inhibitory. In very small amounts, zinc has been reported to be dangerous for oysters and in large amounts to impart a blue-green color. Toward snails, toxic action by zinc has been reported at 1.0 mg/liter in natural water and as low as 0.05-0.10 mg/liter in distilled

Zinc Oxide (ZnO)

No estimates of the acute oral toxicity of zinc oxide were located, and it is assumed that no human fatalities have resulted from ingestion of the pure oxide. Because zinc oxide is soluble in dilute mineral acids (presumably including gastric juice), it probably shares to a limited extent the toxic actions of water-soluble "zinc salts."[2]

Freshly formed fumes of zinc oxide, as from welding, may cause metal fume fever with chills, fever, tightness in the chest, cough and leukocytosis.[1]

C. Environmental Properties

Many zinc salts (e.g. zinc sulfate and zinc chloride) are highly soluble in water; hence it is to be expected that zinc might occur in many industrial wastes.[5] On the other hand, zinc salts such as the carbonate, oxide and sulfide, are insoluble in water and consequently it is to be expected that some zinc will precipitate and be removed readily in most natural waters.[5]

One of the problems with heavy metals is their tendency to concentrate through both aquatic and terrestrial food chains.[22] Aquatic macro- and micro- flora and fauna accumulate heavy metals such as zinc in body tissues in significantly greater concentrations than present in the surrounding environment. These organisms are the food source for fish and insects which retain the zinc in the tissues of the consumed organisms. The fish and insects are consumed in turn by larger organisms; this process continues to the organisms at the top of the pyramidal food chain, such as man and large carnivorous birds and mammals. The more links in the chain, the more severe the bioaccumulation phenomenon.

The drinking water quality standard for zinc is 5.0 mg/liter.[6]

D. Radioactive Properties: None

Zirconium Chloride

A. Chemical/Physical Properties

Zirconyl Chloride ($ZrOCl_2$)

$ZrOCl_2$ in contact with water produces octahydrate, $ZrOCl_2 \cdot 8H_2O$, tetragonal crystals.[1] Zirconyl chloride is freely soluble in water and alcohol.[1] Aqueous solutions behave like solutions of polymers (tetramers) of hydrated $ZrOOH^+$ and chloride ions. The pH is about equal to that of HCl of the same molarity.[1] Aqueous $ZrOCl_2$ solutions have considerable solvent action on sparingly soluble sulfates, such as calcium sulfate, due to removal of sulfate ion from the solution by complexing with the zirconium atom.[1] The free acid in $ZrOCl_2$ solutions may be neutralized, and a solid compound, $ZrOOHCl \cdot nH_2O$ can be recovered. It is highly polymerized in solution and amorphous in the solid state.[1] This compound is mildly acidic and has been used in the preparation of body deodorants and antiperspirant preparations.[1]

The octahydrate, $ZrOCl_2 \cdot 8H_2O$, loses $6H_2O$ at 150°C and $8H_2O$ at 210°C.[4]

B. Biological Properties

So far as is known, the inherent toxicity of zirconium compounds is relatively low. Animal studies indicate neither acute nor systemic injury in response to zirconium compounds given orally for as long as two years.[5] Even 20 percent zirconium oxide in the diet was not harmful. The LD_{50} values for oral administration of zirconium salts to rats, expressed as zirconium, to range from 853 mg/kg of body weight for the nitrate to 2290 mg/kg for sodium zirconyl sulfate.[5] Deaths in rabbits have been caused by zirconium through intravenous injections of relatively large doses on the order of 150 mg/kg body weight.[3]

Most of the zirconium compounds in common use are insoluble and considered to be inert.[3] Pulmonary granuloma in zirconium workers has been reported and sodium zirconium lactate has been held responsible for skin granulomas.[3]

C. Environmental Properties

Although zirconium chloride, nitrate and sulfates are soluble in H_2O, the carbonate, hydroxide, oxide, and silicate are highly insoluble.[5] As a consequence, any dissolved zirconium that reaches natural waters will be precipitated quickly and removed by adsorption or sedimentation.[5]

D. Radioactive Properties: None

References

1. Stecher, P.G., ed. The Merck Index. Rahway, Merck and Co., 1968. 8th edition.

2. Gleason, M., R.E. Gosselin, H.C. Hodge, B.P. Smith. Clinical Toxicology of Commercial Products. Baltimore, The Williams and Wilkins Co., 1969. 3rd edition.

3. Sax, N.I. Dangerous Properties of Industrial Materials. New York, Van Nostrand Reinhold Company, 1968.

4. Hawley, G.G. The Condensed Chemical Dictionary. New York, Van Nostrand Reinhold Company, 1971. 8th edition.

5. McKee, Y.E., H.W. Wolf, eds. Water Quality Criteria. Resources Agency of California State Water Quality Control Board, 1963. 2nd edition.

6. Recommended Methods of Reduction. Neutralization, Recovery or Disposal of Hazardous Waste. Vols I, II, VI, VIII, X, XII, XIII. TRW Systems Group. Redondo Beach, California, 1973.

7. Christensen, H.E., ed. Toxic Substances List, 1973 Edition. U.S. Department of H.E.W. (National Institute for Occupational Safety and Health). Rockville, MD, 1973.

8. Waldbott, G.L. Health Effects of Environmental Pollutants. St. Louis, C. V. Mosby Company, 1973.

9. Handbook of Chemistry and Physics, 52nd edition. Cleveland, The Chemical Rubber Company, 1971-72.

10. Fluorides. Washington, D. C., National Academy of Sciences, 1971.

11. Asbestos, The Need for and Feasibility of Air Pollution Controls. Washington, D. C., National Academy of Sciences, 1971.

12. Chromium. Washington, D. C., National Academy of Sciences, 1974.

13. Buchanan, W.D. Toxicity of Arsenic Compounds. New York, Elsevier Publishing Company, 1962.

14. Water Quality Criteria. Washington, D. C., National Academy of Sciences and National Academy of Engineering, 1972.

15. Burrows, D., J.C. Dacre. Mammalian Toxicology and Toxicity to Aquatic Organisms of White Phosphorus and "Phossy Water." Nashville, Associated Water and Air Resources Engineers, Inc., 1973.

16. Preliminary Investigation of Effects on the Environment of Boron, Indium, Nickel, Selenium, Tin, Vanadium and Their Compounds. Office of Hazardous Materials Control of the Environmental Protection Agency. Springfield, Virginia. Contract #68-01-2215. Versar, Inc., June, 1974.

17. Water Quality Criteria Data Book, Vol. 3: Effects of Chemicals on Aquatic Life. Environmental Protection Agency. U.S. Government Printing Office, Washington, D. C. Contract # 68-01-0007. Battelle's Columbus Laboratories, May, 1971.

18. Pourbaix, Marcel. Atlas of Electrochemical Equilibria in Aqueous Solutions. London (England), Pergamon Press.

19. Manganese. Washington, D. C., National Academy of Sciences, 1973.

20. Dean, J.A., ed. *Lange's Handbook of Chemistry, 11th ed. New York, McGraw-Hill Book Company, 1973.*

21. Jacobs, M.B. *The Analytical Toxicology of Industrial Inorganic Poisons.* New York, Interscience Publishers, 1967.

22. Odum, E.P. *Fundamentals of Ecology.* Philadelphia, W.B. Saunders Company, 1971. 3rd edition.

23. *Public Health Service Drinking Water Standards.* Public Health Service (U.S. Dept. of H.E.W.), 1962.

24. Kosova, L.V. and A.A. Yarosheva. "Action of Niobium Nitride on Animal Organisms".

25. Linke, William, ed. Solubilities of Inorganic and MetalOrganic Compounds. 4th ed. 1958.

APPENDIX B

Private Waste Contractors and Service Organizations

A. Large multi-site integrated hazardous waste contractors

Rollins Environmental Services, Inc. P. O. Box 2349 Wilmington, DE 19899	Integrated multi-treatment complexes and disposal services; 3 sites.
Browning-Ferris Industries, Ind. 300 Fannin Bank Bldg. Houston, TX 77002	Integrated national treatment and disposal facilities; about 100 sites - mostly landfill but including 5 chemical fixation stations.
Waste Management, Inc. 900 Jorie Boulevard Oak Brook, IL 60521	Integrated national treatment and disposal facilities; about 50 sites - mostly landfill.
SGA Services, Inc. 99 High Street Boston, MA 02109	Integrated national treatment and disposal facilities; about 50 sites - mostly landfill, but with waste treatment subsidiaries.

B. Hazardous waste treatment and recovery contractors

Chem-trol Pollution Services, Inc. P. O. Box 200 Model City, NY 14107	Liquid treatment and secured landfill disposal.
Hyon Waste Treatment Services Chicago, IL 60607	Integrated waste treatment facility - biological, chemical incineration.
Chemical Control Corp. Elizabeth, NJ 07207	Liquid and solid chemical processing and incineration.
Conservation Chemical Co. P. O. Box 6066 Gary, IN 46406	Treatment and disposal of liquid and hazardous wastes.

Conservation Chemical Co. P. O. Box 6304 Kansas City, MO 64126	Treatment and disposal of liquid and hazardous wastes.
Industrial Waste Disposal Co., Inc. Dayton, OH 45401	Treatment and disposal plant.
Nelson Chemical Co. 12345 Schaefer Highway Detroit, MI 48227	Wet chemical treatment of cyanides, chrome, plating solutions and similar wastes amenable to this approach.
Evor Phillips Leasing Co. Old Bridge, NJ 08857	Industrial liquid transportation and treatment - ocean disposal.
Erieway Pollution Control, Inc. 33 Industry Drive Cleveland, OH 44101	Industrial waste treatment and chemical fixation.
Industrial Tank, Inc. 210 Berrellesa Street P. O. Box 831 Martinez, CA 94553	Liquid transporting, treatment, and disposal; Class I hazardous waste disposal sites, State of CA.
Bio-Ecology Systems, Inc. 4100 E. Jefferson Avenue Grand Prairie, TX 75050	Liquid treatment of metal processing wastes (plating etc) chemicals, acids, incineration.
Systems Technology Franklin, OH 45005	Hazardous waste treatments.
Environmental Waste Control, Inc. 26705 Michigan Avenue Inkster, MI 48141	Liquid treatment of acids, alkalies, pickle liquor.
Western Processing Co. Kent, WA 98031	Contractor for chemical reclamation.
Pollution Controls, Inc. P. O. Box 238 Shacopee, MN 55379	Incineration and liquid waste treatment.
Pollution Abatement Wastes Oswego, NY 13126	Industrial waste disposal; landfill and incineration.

Aztec Mercury P. O. Box 1676 Alvin, TX 77511	Mercury recovery from industrial wastes.
Wood Ridge Chemical Corp. Division of Troy Chemical Co. Park Place East Wood Ridge, NJ	Reprocessors of mercury wastes.
SGC Industries Old Bridge, NJ 08857	Chemical fixation processes.
Renner, Inc. Box 3224 Port Arthur, TX 77640	Landfilling and chemical fixation.
Environmental Sciences, Inc. Chemfix Division 505 McNeilly Road Pittsburgh, PA 15226	Chemical fixation on-site and off-site mobile treatment units.

C. General purpose landfill contractors and services

Koski Construction Co. 5841 Woodman Avenue Ashtabula, OH 44004	Impervious base settling pond.
Knickerbocker Landfill Malvern, PA 19355	Lined landfill.
Pottstown Disposal Services Pottstown, PA 19464	Lined landfill.
Scientific Inc. 17 E. Second Street Scotch Plains, NJ 07076	Landfill operators accepting liquids.
Sanitas Waste Disposal of MI 15500 Schaeffer Road Detroit, MI	Contractor for disposal in commercial landfill.
Tork Construction Wisconsin Rapids, WS 54494	Contractor for disposal in private landfill.

D. General purpose secured landfill contractors and services

Nuclear Engineering Co., Inc. Hurstbourne Park 9200 Shelby Road Louisville, KY 40222	Primarily nuclear waste disposal; hazardous containerized waste burial plus some liquid chemical treatment; 3 sites.
Wescon, Inc. P. O. Box 564 245 Third Avenue E. Twin Falls, IA 83301	Hazardous wastes secured disposal.
Industrial Hazardous Waste Land Disposal Site Route 2 Lindsay, OK 74052	Hazardous materials landfill.
Resource Recovery Corp. Pasco, WA 99301	Interrelated companies - liquid, sludge and solid hazardous chemical disposal by evaporation plus secured landfill.
Chemical Processors, Inc. 5501 Airport Way South Seattle, WA 98108	See above
County Sanitation Districts of Los Angeles County 2020 W. Beverly Boulevard Los Angeles, CA 90057	Municipal Class I disposal sites; State of CA.
Ventura Regional County Sanitation District 181 S. Ash Street Ventura, CA 93001	Municipal Class I disposal site - State of CA.
Wescon, Inc. P. O. Box 564 245 Third Ave., E. Twin Falls, IA 83301	Hazardous waste disposal; abandoned missile base.

E. Deep Welling Contractors

Sonics International P. O. Box 47086 Dallas, TX 75247	Deep welling of acids and other chemicals.
U.S. Pollution Control, Inc. 5024 S. Quaker Tulsa, OK 74101	Contractor for disposal of hazardous industrial wastes deep well and landfill.

F. Ocean Disposal Contractors

Modern Transportation Kearney, NJ 07032	Ocean disposal.
Safety Products and Engineering 3 Malden Street W. Quincy, MA 02169	Ocean disposal hazardous waste.

G. Solid Waste Consultants

Chemical Buyers Service, Inc. P. O. Box 2065 Berkeley, CA 97400	Chemical recycling contractors.
International Hydronics Princeton, NJ 08540	Consulting process engineers for waste treatment facilities.
Emcon Associates 326 Commercial Street San Jose, CA 95112	Environmental consultants - landfill geology and design.

H. Miscellaneous Services

Quality Septic Tank Service A & B Quality Drain Service Capital Heights, MD 20027	Contractors for waste sludge hauling.
Contee Sand & Gravel Co., Inc. Box 460 Laurel, MD 20810	Land disposal.

Appendix C

Cost Conversion Indices

Costs for treatment and disposal reported herein were based on mid-1973 pricing. Table C-1 presents applicable indices (or estimates) for converting to December 1973 dollars. Based on this table, we estimate the average cost increase to be approximately +4% between the two dates. The price increase for particular cost elements (i.e. land, labor, energy, etc.) may be applied individually for those treatment/disposal situations in which the total is particularly influenced by an element which varies significantly from the 4% average. In light of the goal of ± 25% accuracy for most cost estimates, we do not believe such corrections to be significant.

Table C-1

Comparison of Costs, June, 1973 and Dec., 1973

			Index	
Element	**Source**	**Jn. 73**	**Dc. 73**	**Change**
Construction	CE Plant Cost Index	144.5	148.2	+ 2.6%
	Boeckh Index (Commercial & Factory Bldgs.)	155.3	157.7	+ 1.0%
Equipment	M&S Equipment Cost	342.9*	349.5**	+ 1.9%
Energy	Wholesale Price Index (BLS)			
Gas Fuels		128.0	137.6	+ 7.5%
Electric Power		128.4	135.9	+ 5.8%
Petroleum Prod., Refined		146.6	252.0	+ 71.9%
Labor	Hourly Earnings Current Labor Statistics, (BLS)			
Contract Construction		6.35	6.70	+ 5.5%
Chemicals & Allied Products		4.46	4.60	+ 3.1%
Transportation	No applicable index found	----	----	+ 5-10% (est.)
Land	Telecon; Soc. of Ind. Realtors	----	----	+ 5% (est)

*2nd Quarter '73 **4th Quarter '73

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